

**The 10<sup>th</sup> International Conference on**  
***Intergranular and Interphase***  
***Boundaries***

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*July 23 – 26, 2001*  
*Haifa Israel*

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## *Intergranular and Interphase Boundaries*

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*D. Brandon (Chairperson)*

*E. Rabkin (Treasurer)*

*R. Shneck (Program)*

*W.D. Kaplan (Secretary)*

**iib2001 –Program**

Session	Day	Title
I	Monday AM	Interfacial Structure & Defects
II	Monday PM	Electronic Structure at Interfaces
III	Monday PM	Interfaces in Nano-Structures
IV	Tuesday AM	Solid-Liquid Interfaces & Wetting
V	Wednesday AM	Solid-Liquid Interfaces & Wetting...continued
VI	Wednesday PM	Segregation
VII	Wednesday PM	Grain Boundary & Interface Ensembles
VIII	Thursday AM	Interface Energy & Morphology
IX	Thursday PM	Interface Diffusion & External Fields
X	Thursday PM	Interface Motion & Dynamics

**Monday, July 23**

**9:00            Opening Session & Introductory Remarks, David Brandon,  
Conference Chairperson**

**Session I:        Interfacial Structure & Defects**

- 9:30            Keynote    M.W. Finnis, A. Y. Lozovoi and A. Alavi,  
*The Energetics of Alumina Surfaces and Thin Oxide films on NiAl*
- 10:15                            I. Goldfarb, L. Banks-Sills, R. Eliasi, and G.A.D. Briggs,  
*Finite Element Analysis of CoSi<sub>2</sub> Nanocrystals on Si(001)*
- 10:45                            Coffee Break
- 11:15                            G.A. Frank, R. Z. Shneck, A. Landau, and A. Venkert,  
*Subgrains Analysis in  $\alpha$ -Uranium Using Combined TEM and Single  
Crystal Plasticity Theory*
- 11:45                            A. Béré and A. Serra,  
*Atomic Structure of [0001] Tilt Boundaries in GaN*
- 12:15                            LUNCH

**Session II:        Electronic Structure at Interfaces**

- 13:30            Keynote    D.N. Seidman, J.T. Sebastian, R. Benedek, and O.C. Hellman  
*Atomic-Scale Studies of Ceramic/Metal Heterophase Interfaces:  
Structure, Chemistry, and Bonding*

- 14:15      Keynote      C. Scheu, G. Dehm, T. Wagner and M. Rühle  
*Influence of the Substrate Preparation on the Atomic and Electronic Structure of Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Interfaces*
- 14:45                      Y. Tsur  
*Kinetic Considerations in the Formation of Electrical Active Grain Boundaries in Barium Titanate and Similar Perovskites*
- 15:15                      J.M. Carlsson, H.S. Domingos, B. Hellsing and P. Bristowe  
*Electronic Structure of a Bi-Doped  $\Sigma=13$  Tilt Grain Boundary in ZnO*
- 15:45                      Coffee Break

### **Session III:    Interfaces in Nano-Structures**

- 16:15      Invited      Y. Estrin  
*Inhibition of Grain Growth by Vacancy Generation*
- 16:45                      Y. Ashekanzy, K. Albe, and R.S. Averback  
*Spontaneous Nanocluster Rotation*
- 17:15                      E. Katz, S. M. Tuladhar, A.I. Shames, S. Shtutina, and D. Faiman  
*Grain Boundary Diffusion in C60 Thin Films*
- 17:45                      A. Rothschild, Y. Komem, and F. Cosandey  
*The Impact of Grain Boundary Diffusion on the Low Temperature Oxidation Mechanism in Nanocrystalline TiO<sub>2-x</sub> Thin Films*
- 20:30                      Music & Dance Show

<b>Tuesday, July 24</b>
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### **Session IV:    Solid-Liquid Interfaces & Wetting**

- 8:30      Keynote      J. Cahn  
*Wetting and Wetting Transitions in Fluids and Solids*
- 9:15      Keynote      R. Yerushalmi-Rozen, T. Kerle, and J. Klein  
*Alternative Pathway of Dewetting at the Liquid/Liquid Interface*
- 10:00      Keynote      S. Weiner, L. Addadi and D.H. Wagner  
*Design Strategy of Multi-Functional Biological Materials*
- 10:45                      Coffee Break

- 11:15 J.-P. Monchoux, E.Y. Gutmanas, and E. Rabkin  
*Energetics and Kinetics of Surfaces and Interfaces in Fe-Pb System*
- 11:45 A. Hashibon, J. Adler, M.W. Finnis, and W.D. Kaplan  
*Atomistic Study of Structural Correlations at a Model Liquid-Solid Interface*
- 12:15 K. Wolski, N. Marié, V. Laporte, and M. Biscondi  
*About The Importance of Nanometer-Thick Intergranular Penetration in the Analysis of the Liquid Metal Embrittlement Mechanisms*
- 14:30 Tour to Acco and Yehiam Fortress. Dinner under the stars at Yehiam.

<b>Wednesday, July 25</b>
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**Session V: Solid-Liquid Interfaces & Wetting.....continued**

- 9:00 Keynote D. Chatain, P. Wynblatt, S. Hagège, E.J. Siem, and C. Carter  
*Wetting in Multiphase Systems with Complex Geometries*
- 9:45 W. Ludwig, D. Bellet, S.F. Faester, H.F. Poulsen, and J. Susini  
*Possibilities of Synchrotron Radiation Imaging Techniques for the Study of Grain Boundary Related Phenomena*
- 10:15 Coffee & Posters
- 10:45 M. Eggersmann, F. Ye, O. Gutfleisch, and R. Würschum  
*Intergranular Melting of Nanocrystalline Nd<sub>2</sub>Fe<sub>14</sub>B Studied by Means of Radiotracer Diffusion*
- 11:15 H. de Monestrol, L. Schmirgeld-Mignot, S. Poissonnet, Ch. Lebourgeois and G. Martin  
*Reactive Solid State Dewetting: Cavity Nucleation in the System Ag-Ni-O*
- 11:45 LUNCH

**Session VI: Segregation**

- 13:30 Keynote P. Lejcek, and S. Hofmann  
*On the Relationship Between Enthalpy and Entropy of Grain Boundary Segregation*
- 14:15 A. Umantsev, Continuum  
*Theory of Interfacial Segregation*

14:45 D. Isheim and D.N. Seidman  
*Atomic-Scale Structure and Chemistry of Segregation at Heterophase Interfaces*

15:15 Coffee & Posters

### **Session VII: Grain Boundary & Interface Ensembles**

15:45 Keynote G. Gottstein, D.A. Molodov, M. Winning, and L.S. Shvindlerman  
*Grain Boundary Dynamics: a Novel Tool for Microstructural Control*

16:30 G. Dehm, T.J. Balk, B.J. Inkson, T. Wagner, and E. Arzt  
*Interface Controlled Plasticity in Thin Metal Films*

17:00 D. Weygand, J. Lépinoux, and Y. Bréchet  
*Nucleation of Recrystallization: A Vertex Dynamics Approach*

17:30 N.K. Tsenev, and A.M. Shammazov  
*Structure of Grain Boundaries and Mechanical Behaviour of Submicrocrystalline Aluminium Alloys*

18:00 F. Muktepavela, and J. Maniks  
*Structure Evolution and Diffusion During Interphase Boundary Sliding in Sn-Based Binary Eutectics*

18:30 Beer & Posters

*Free Evening*

<b>Thursday, July 25</b>
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### **Session VIII: Interface Energy & Morphology**

9:00 Keynote E. Rabkin and L. Klinger  
*Effects of Surface Anisotropy on Grain Boundary Grooving*

9:45 Keynote P. Wynblatt, M. Takashima, B.L. Adams and A.D. Rollett  
*Correlation of Grain Boundary Character with Wetting Behavior*

10:30 Coffee Break

11:00 B.B. Straumal, S.A. Polyakov, E. Bischoff, W. Gust, and E.J. Mittemeijer  
*Faceting of  $\Sigma 3$  and  $\Sigma 9$  Grain Boundaries in Copper*

11:30 W. Sigle, L.-S. Chang, W. Gust and M. Rühle  
*On the Correlation between Grain Boundary Segregation, Faceting  
and Embrittlement in Bi Doped Copper*

12:00 LUNCH

## Session IX: Interface Diffusion & External Fields

13:30      Keynote    C.A. Volkert, J. Böhm, R. Mönig, J. Nucci, A. Straub, C. Witt,  
and E. Arzt  
*Effect of Diffusion Path on Electromigration-Induced Damage*

14:15 S. Divinski, M. Lohmann, and C. Herzig  
*Effect of Tracer Atoms on Grain Boundary Motion during Ag and Cu*  
*Grain Boundary Diffusion in Cu Polycrystals*

14:45 P. Zieba and W. Gust  
*On the Activation Energy of the Diffusion Process at Migrating Grain Boundaries*

15:15 E. E. Glickman  
*Electromigration in Microelectronic Interconnects: Coupling  
Interface Electrotransport to Interface Reactions*

15:45 Coffee Break

## Session X: Interface Motion & Dynamics

16:15      Keynote    D. J. Srolovitz, M. Upmanyu, L. S. Shvindlerman, and G. Gottstein  
*Triple Junction Migration*

17:00	Invited	<u>L. S. Shvindlerman</u> , G. Gottstein, D.A. Molodov, and V.G. Sursaeva <i>Triple Junction Motion in Metals</i>
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17:30 D. A. Molodov, P. Konijnenberg, W. Hu, G. Gottstein,  
and L. S. Shvindlerman  
*Effect of Dislocation Absorption on the Motion of Specific Grain  
Boundaries in Al-Bicrystals*

18:00 M. Upmanyu, D.J. Srolovitz, W. C. Carter, A. Lobovsky, J. A. Warren  
and R. Kobayashi  
*Simultaneous Grain Boundary Migration and Grain Rotation*

18:30 **Closing Discussion & Summary**  
*David Seidman, David Srolovitz, David Brandon*

**20:30 Gala Dinner**

## **The Energetics of Alumina Surfaces and Thin Oxide Films on NiAl**

M. W. Finnis, A. Y. Lozovoi and A. Alavi

*Atomistic Simulation Group  
School of Mathematics and Physics  
Queen's University Belfast  
Belfast BT7 1NN  
Northern Ireland  
<http://titus.phy.qub.ac.uk>*

Using a formalism developed for studying the surface free energy of alumina[1-2], the early stages of oxidation of NiAl(110) have been studied by a combination of total energy calculation, using a first-principles pseudopotential method, and thermodynamic modelling[3-4]. The structures and energies of a number of surface compositions with from 1/3 monolayer to two layers of oxygen have been calculated. The main driving force is the affinity of Al for O, and the lowest energy oxidelayers are formed by incorporating Al from the substrate. For such thin oxide layers, the free energy has to be obtained by treating them as complicated surfaces, that is without making a distinction between oxide-metal and metal-vapour interfacial energies. The free energies of the surfaces depend on the chemical potentials of the three components and are expressed in terms of the partial pressure of oxygen, the temperature and the stoichiometry of the substrate. Significant differences in the relative energies of oxidised surfaces are obtained depending on whether or not point defects in the surface layers of NiAl are present to deliver Al to the oxygen. In both cases we find the energy in ambient conditions to be a *decreasing* function of oxygen coverage.

The difference becomes apparent in the relative energetics of a thin unbroken layer versus thicker islands. With point defects present, for the same total amount of adsorbed oxygen the energy of a double layer of oxide is lower than that of a single layer, whereas without point defects the reverse is the case. This suggests that on thermodynamic grounds island growth would generally be favoured over layer-by-layer growth of films at high temperature such that aluminium transport to the surface can take place.

- [1] I. G. Batyrev, A. Alavi and M. W. Finnis, "Ab initio calculations on the Al<sub>2</sub>O<sub>3</sub>(0001) surface." *Faraday Discuss.* **114**, 33-43 (2000).
- [2] I. G. Batyrev, A. Alavi and M. W. Finnis, "Equilibrium and adhesion of Nb/sapphire: the effect of oxygen partial pressure." *Phys. Rev. B* **62**, 4698-4706 (2000).
- [3] A. Y. Lozovoi, A. Alavi and M. W. Finnis, "Surface stoichiometry and the initial oxidation of NiAl(110)." *Phys. Rev. Lett.* **85**, 610-613 (2000).
- [4] A. Y. Lozovoi, A. Alavi and M. W. Finnis, "Surface energy and the early stages of oxidation of NiAl(110)." *Computer Physics Communication* to appear. (2001).

## **Finite Element Analysis of CoSi<sub>2</sub> Nanocrystals on Si(001)**

I. Goldfarb<sup>1</sup>, L. Banks-Sills<sup>1</sup>, R. Eliasi<sup>1</sup>, and G.A.D. Briggs<sup>2</sup>

<sup>1</sup>*Department of Solid Mechanics, Materials and Systems*

*The Fleischman Faculty of Engineering*

*Tel Aviv University, Ramat Aviv 69978, Israel*

<sup>2</sup>*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK*

Cobalt disilicide (CoSi<sub>2</sub>) is important for self-aligned contact and interconnect material, as well as for metal-based transistors and detectors. High-quality smooth epitaxial silicide layers could yield numerous advantages for such applications, especially on the preferred Si(001) surface. However, precisely on this surface three-dimensional (3D) islands result instead, whether in reactive or molecular beam epitaxy. This phenomenon is somewhat surprising, as 3D growth (which is commonly presumed to be stabilized by the relaxation of mismatch strain by the 3D islands) is not expected at such low mismatch values as 1.2% that exists at the CoSi<sub>2</sub>/Si interface.

In this work we present finite element analysis of pyramidal and hut-shaped CoSi<sub>2</sub> nanocrystals reactively deposited onto the Si(001) substrates. These dots have been observed by us, as well as by other groups. Our analyses show that elastic strain relaxation by the 3D nanoislands is not the stabilizing factor, at least not at the experimentally observed volumes. This concurs the well-accepted theory, which predicts higher 3D nucleation barrier and critical nucleus size at lower mismatch values. Hence, alternative explanations for the 3D growth of CoSi<sub>2</sub> nanocrystals are proposed.

## **Subgrains Analysis in $\alpha$ -Uranium Using Combined TEM and Single Crystal Plasticity Theory**

G. A. Frank<sup>1</sup>, R. Z. Shneck<sup>1</sup>, A. Landau<sup>2</sup>, A. Venkert<sup>2</sup>

*1- Dept. of Materials Engineering, Ben-Gurion University of the Negev, P.O.Box 653, Beer-Sheva 84105, Israel.*

*2- Nuclear Research Center Negev, P.O.Box 9001, Beer-Sheva Israel.*

Fragmented morphology is typical in  $\alpha$ -Uranium grains formed by a diffusional  $\beta \rightarrow \alpha$  phase transformation. These subgrains are easily found by optical microscopy. It is believed that these subgrains are dislocation cells, which form during plastic deformation of the  $\alpha$  phase. Plastic deformation can evolve due to the volume and shape change accompanying the  $\beta \rightarrow \alpha$  transformation. The main effort to verify this assumption was done by Cahn & Tomlinson, who determined some geometric parameters of several boundaries and showed that they can be explained as boundaries formed by the dislocations inherent to  $\alpha$ -Uranium.

The exploration of dislocation patterning into walls renews the interest in subgrains of Uranium. A major difficulty encountered in the analysis of dislocations cells in cubic metals is the multiplicity of active slip systems. The low symmetry of  $\alpha$ -Uranium simplifies this problem. In the present work we take advantage of this property to try and verify the assumption that the subgrains structure found after plastic deformation is composed of the gliding dislocations.

U-0.1%Cr samples were heat treated at 720°C ( $\beta$ -phase) for 0.5 hours and then furnace cooled to room temperature. The samples were examined using optical and scanning electron microscopy followed by TEM characterization. The sub-boundaries were analyzed by SAD in order to determine their rotation vectors ( $R$  and  $\omega$ ). The direction normal to each boundary ( $n$ ) was estimated.

Using single crystal plasticity theory, the yield surface of  $\alpha$ -Uranium was calculated to predict the relative activity of each slip system for any plastic strain. The stresses prevailing in a newly formed  $\alpha$  particle were calculated by solving the elasto-plastic inclusion problem. The state of stress and the yield surface were used to determine the combination of active slip systems by the maximum external energy principle.

The conformance between the predicted set of gliding dislocations and the boundaries characteristics ( $R, \omega n$ ) observed by TEM is examined using the Frank-Bilby equation. Frank-Bilby equation relates the dislocation contents in the boundary to its geometrical characteristics ( $R, \omega, n$ ).

The TEM results will hopefully provide experimental evidence connecting the active slip systems during plastic deformation and the dislocation contents of the subgrain boundaries.

## **Atomic Structure of [0001] Tilt Boundaries in GaN**

Antoine Béré and Anna Serra

*Departament de Matemàtica Aplicada III, Universitat Politècnica de Catalunya, Jordi Girona,  
1-3 Barcelona, Spain*

Crystals of GaN grown by molecular-beam epitaxy on (0001) sapphire show [0001] tilt boundaries of low and high angles [1]. The structure of these boundaries plays a role in the optoelectrical properties shown by this semiconductor. In this work we have studied the atomic structure of  $\Sigma 7$ ,  $\Sigma 13$  and  $\Sigma 19$  boundaries (in the coincidence site lattice notation) by means of atomic computer simulation using a modified version of the empirical Stillinger-Weber interatomic potential.

For each  $\Sigma$  boundary we studied the interface of lowest period and found the atomic structure of minimum energy by applying the method of quasidynamic relaxation. In the case of  $\Sigma 13$  we have studied different interfaces comparing our results with the experimental results obtained in a study of bicrystals of ZnO [2]

In some boundaries the atomic structure can be understood in terms of edge dislocations located along the boundary. Edge dislocations in bulk GaN have been studied with the same potential and the stable structures are presented here for comparison.

1. V.Potin, P.Ruterana, G.Nouet, R.C.Pond and H.Morkoç; *Physical Review B*, **61**, 5587
2. A.N.Kiselev, F.Sarrazit, E.A.Stepantsov, E.Olsson, T.Claeson, V.I. Bondarenko, R.C.Pond and N.A. Kiselev; *Phil Mag. A*, **76**, 633

## Atomic-Scale Studies of Ceramic/Metal Heterophase Interfaces: Structure, Chemistry, and Bonding

David N. Seidman<sup>1</sup>, Jason T. Sebastian<sup>1</sup>, Roy Benedek<sup>1</sup>, and Olof C. Hellman<sup>1,2</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3108 U.S.A.*

<sup>2</sup>*ScenicSoft, Inc., Lynnwood, Washington 98037-8192 U.S.A.*

Experimental research on ceramic/metal (C/M) interfaces that utilizes transmission electron, high-resolution electron, Z-contrast, and atom-probe field-ion microscopies, and electron energy-loss spectroscopy (EELS), in conjunction with *ab initio* atomistic modeling and molecular dynamics (MD) simulations, is presented. Extensive use is made of atom-probe microscopy (APFIM) and three-dimensional (3DAPM) and EELS to address questions concerning the chemistry of the terminating polar plane (anion versus cation) and segregation of different solute species to C/M interfaces. Detailed experimental results have been obtained for the {222}MgO/Cu, {222}CdO/Ag [1], {222}MgO/Cu(Ag) [2], {222}CdO/Ag(Au) [3] and Sb at MnO/Ag [4] heterophase interfaces. All the ceramic/metal interfaces were created employing internal oxidation of high-purity binary or ternary metallic alloys, thereby producing atomically clean heterophase interfaces. Solute segregation was induced at C/M interfaces by annealing specimens containing a ternary addition at a low temperature to induce segregation. The Gibbsian interfacial excess is determined directly by APFIM or 3DAPM [4,5]. Results concerning *ab initio* atomistic modeling of the {222}MgO/Cu coherent interface (zero-misfit approximation), using local density functional theory within the plane-wave pseudopotential framework, for two polar (111) and two nonpolar (100) MgO/Cu interfaces and are compared with our experimental observations [6,7]. MD simulations of the dislocation structure of the {222}MgO/Cu are compared with STEM observations [7]. EELS is used to measure directly the electronic states of this interface. O K and Cu L<sub>2,3</sub> edges show the formation of metal-induced gap states (MIGS) within the band gap of MgO, at the interface [8,9]. Both theory and experiment find the MIGS to be strongly localized at the interface, resulting in a small interface core-level shift.

- [1] D. K. Chan, D. N. Seidman, and K. L. Merkle, *Phys. Rev. Lett.* **75**, 1118 (1995).
- [2] D. A. Shashkov and D. N. Seidman, *Phys. Rev. Lett.* **75**, 268 (1995).
- [3] D. A. Shashkov, D. A. Muller, and D. N. Seidman, *Acta Mater.* **47**, 3953 (1999); J. T. Sebastian *et al.*, to appear in *Materials Research Society Proceedings* (2001).
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- [6] R. Benedek, M. Minkoff, and L. H. Yang, *Phys. Rev. B* **54**, 7697 (1996).
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## **Influence of the Substrate Preparation on the Atomic and Electronic Structure of Cu/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Interfaces**

Christina Scheu, Gerhard Dehm, Thomas Wagner and Manfred Rühle

*Max-Planck-Institut für Metallforschung, Stuttgart, Germany*

In the present study, Cu films were grown on (0001) oriented, single-crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates by molecular beam epitaxy (MBE) (base pressure  $p \leq 10^{-8}$  Pa) at a substrate temperature of 600°C. Prior to deposition, the polished (0001) oriented  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystals were chemically cleaned and then directly annealed for 1 hour at 1000°C in the ultra-high vacuum (UHV) chamber. The surface was then sputtered for 10 minutes using 1 keV Ar<sup>+</sup> ions, followed by a second annealing for 2 hours at 1000°C in UHV. The results obtained for this specimen are compared to earlier studies on Cu/(0001) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> interfaces prepared by MBE where the (0001) oriented, single-crystalline  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates were chemically cleaned and annealed for 2 hours at 1200°C in UHV, without using an additional Ar<sup>+</sup>-sputtering process [1-3].

High-resolution transmission electron microscopy investigations revealed that both Cu/(0001)Al<sub>2</sub>O<sub>3</sub> interfaces possess a epitaxial orientation relationship and that the interfaces are atomically abrupt. No reaction phases form at the interfaces due to the ultra high vacuum conditions used during film growth. The electronic structure of the interfaces was investigated by an analysis of the energy-loss near-edge structure (ELNES) associated with each absorption edge in electron energy-loss spectroscopy data.

For the Cu/(0001)Al<sub>2</sub>O<sub>3</sub> interface, where the Al<sub>2</sub>O<sub>3</sub> substrate was Ar<sup>+</sup>-sputter cleaned prior to the deposition, Cu-Al bonds occur. This is indicated by the existence of an interfacial Al-L<sub>2,3</sub>-ELNES which reveals that the Al atoms participate in the bonding and that they change their local coordination compared to bulk Al<sub>2</sub>O<sub>3</sub>. Furthermore, the interfacial Cu-L<sub>2,3</sub>-ELNES shows a chemical shift of the edge onset by  $1.8 \text{ eV} \pm 0.3 \text{ eV}$  to higher energy-loss values compared to metallic Cu and the existence of unoccupied Cu-3d states. The shape and edge onset are similar to the Cu-L<sub>2,3</sub>-edge measured in an intermetallic CuAl<sub>2</sub> compound confirming Cu-Al bonds at the Cu/(0001)Al<sub>2</sub>O<sub>3</sub> interface. In addition to the interfacial Al-L<sub>2,3</sub>-ELNES and Cu-L<sub>2,3</sub>-ELNES, there is also an interfacial O-K-ELNES which has a different shape compared to bulk Al<sub>2</sub>O<sub>3</sub>. This is due to a change of the medium-range oxygen environment at the interface. The Cu/(0001)Al<sub>2</sub>O<sub>3</sub> specimen, where the Al<sub>2</sub>O<sub>3</sub> substrate was not Ar<sup>+</sup>-sputter cleaned but annealed at a higher temperature before the Cu was deposited, showed a different bonding behaviour [3]. The ELNES studies revealed Cu-O bonds with mixed ionic-covalent character and some charge transfer from the interfacial Cu atoms to the O atoms of the Al<sub>2</sub>O<sub>3</sub> substrate [3].

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## **Kinetic Considerations in the Formation of Electrical Active Grain Boundaries in Barium Titanate and Similar Perovskites**

Yoed Tsur

*Department of Chemical Engineering, Technion, Haifa, Israel*

Grain boundaries in ceramic barium titanate and related materials can be engineered in order to obtain desired transport behavior. Our ability to do so is closely related to kinetic limitations during the preparation. The close-packed structure of perovskites excludes native or foreign interstitials in the bulk. (Interstitial protons are regarded as  $OH_o^\bullet$ , using the Kröger-Vink notation). Antisites are also unlikely due to size, charge and coordination number mismatch. The possible point defects are, therefore, substitutionals and vacancies. The kinetic limitations of these species, and the results in terms of grain boundary engineering, are considered in this presentation.

A clear distinction between three different conditions is made. At very high temperature, it is assumed that all the relevant defects are mobile and can equilibrate, at least locally. Hence, their concentrations are all functions of the degrees of freedom of the system. At lower temperatures, the cation sublattice is frozen. Therefore, the concentrations of metal vacancies and substitutional cations are constants and, from local neutrality point of view, a new parameter becomes important: the concentration of frozen charge. The concentrations of electronic defects and oxygen vacancies in this metastable state are functions of the temperature, the oxygen partial pressure and the frozen charge. The normalized concentration of frozen metal vacancies is calculated as a function of the doping factor,  $f$  (defined as the ratio between the electron concentration at a given state and at a reference state), and a nonstoichiometry parameter. Around room temperature, the anion sublattice is also frozen, and only electrons and holes exhibit significant transport properties.

The analysis is done in two steps. First, analysis of charge-compensation mechanisms of doped alkaline earth titanates is presented, assuming equilibrium. An analytic expression for the total frozen ionic charge in the metastable state is given. Then, the effects of spatial distribution of the defects are considered.

Possible routes to control the grain boundary properties, based on educated control of the various degrees of freedom during the preparation are discussed.

## **Electronic Structure of a Bi-doped $\Sigma=13$ tilt grain boundary in ZnO**

Johan M. Carlsson<sup>1</sup>, Helder S. Domingos<sup>2</sup>, Bo Hellsing<sup>1</sup> and Paul Bristowe<sup>2</sup>

<sup>1</sup>*Experimental Physics, School of Physics and Engineering Physics,  
Chalmers and Göteborg University, SE-412 96 Gothenburg, Sweden*

<sup>2</sup>*Department of Materials Science and Metallurgy, University of Cambridge,  
Pembroke street, Cambridge CB2 3QZ, UK.*

The Varistor is a voltage dependent resistor which is used for protection of sensitive devices in power applications and circuit constructions. The voltage dependence is very strong, particularly in the breakdown region where the current increases several orders of magnitude. The Varistors are multi-component materials made from polycrystalline ZnO with a number of additives as Bi and Sb. It is generally believed that interface states in the grain boundaries in these materials are responsible for the non-linearity and that the additives enhances the effect. The local electronic structure of grain boundaries in ZnO is therefore of interest in order to understand the mechanism responsible for the varistor behaviour.

We have investigated a  $\Sigma=13$  tilt grain boundary in ZnO by *ab-initio* DFT-calculations using a GGA exchange-correlation functional and ultrasoft pseudopotentials.

We obtained two stable geometries for the  $\Sigma=13$  tilt grain boundary. The structural units of the higher energy geometry was similar to the HREM electron microscopy observations for a  $\Sigma=13$  tilt grain boundary in ZnO. This clean grain boundary had two dangling bond states per structural unit close in energy to the top valence band. These findings were not sufficient to explain the non-linearity in commercial Varistors. We have therefore extended the investigation considering doping in bulk and the  $\Sigma=13$  grain boundary.

In a recent study of Sb doping of a grain boundary [1] we found a strong preference for segregation to the grain boundaries and that the Sb-atoms induced localized states in the grain boundary. Bi is isovalent to Sb, but since Bi is located one row below Sb in the periodic system, the Bi atom is larger than Sb. This leads to an even stronger preference for segregation for the Bi-atoms compared to the Sb-atoms. The Bi-atom also induced localized states both in the bulk and in the grain boundary.

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## **Inhibition of Grain Growth by Vacancy Generation**

Yuri Estrin

*IWW, TU Clausthal, Germany*

It has often been observed that ultra fine grained materials are more stable against grain growth than expected on the basis of the grain boundary mobility and the boundary energy as the driving force for grain growth. It has been suggested that vacancy generation accompanying grain growth acts as an inhibiting factor. In this talk, this inhibition effect of vacancies discussed in a series of papers co-authored by G. Gottstein, L.S. Shvindlerman, E. Rabkin and the speaker<sup>1-4</sup> will be presented. It is assumed that the excess free volume of grain boundaries that is liberated as a result of grain growth is accommodated in the form of vacancies. This kinetically necessary vacancy generation is shown to give rise to inhibition of grain growth in ultra fine grained bulk materials and thin films. Critical conditions for the occurrence of this effect, particularly with respect to the initial grain size and temperature, are obtained. Some predictions of the model, e.g. the occurrence of *linear* grain growth controlled by the coefficient of self-diffusion, have been recently confirmed by experiment. Other salient features of the inhibition mechanism, such as a pronounced vacancy supersaturation during linear grain growth, await experimental validation. Of interest is also the development of tensile stresses in thin films and multilayers during grain growth: a linear increase of stress during linear grain growth, followed by saturation during subsequent parabolic growth, has been predicted.

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## **Spontaneous Nanocluster Rotation**

Yinon Ashekanzy<sup>(1,2)</sup>, Karsten Albe<sup>(1,2)</sup>, R.S. Averbach<sup>(1,2)</sup>

<sup>(1)</sup>*Center for simulation of advance rockets,  
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

<sup>(2)</sup>*Materials research Laboratory,  
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

The behavior of metallic-nanoparticles on surface is becoming of increased scientific and technological interest as new applications for these ultra-small particles are discovered and new methods for synthesizing them are developed. Owing to their small size, however, they are difficult to examine by experimental means and computer simulations are becoming an attractive alternative.

In this work we employ molecular dynamics to elucidate the structure and dynamics of Pt nanoparticles on Pt surfaces. We choose simple symmetric twist boundaries for study since they afford a complete analysis of the grain boundary behavior. The relaxed structure of these boundaries when a small cylinder is placed in twist alignment is an array of dislocations, of a mixed character for most orientations as described for interface boundaries. A model of a dislocation array of the interface was investigated.

These dislocations however interact with the nearby grain surfaces and for nanoparticles smaller than  $\approx 15$  nm in diameter; this interaction leads to dissociation of the dislocations, which does not happen in the bulk. Moreover, when the particle size falls below  $\approx 6$  nm, the interaction becomes so strong that the dislocations glide athermally to the particle surface, leading to the rotation and the crystallographic alignment of the nanoparticles on the surface. For larger particles only the outer dislocations can glide to the surface leading to partial rotation.

We have constructed from hundreds of simulations orientations maps outlining the dependence of full and partial rotation of nanoparticles on particle diameter and height, temperature, and initial twist angle. From comparisons of the rotation behavior of twist boundaries on three different interfaces, conclusions about the general behavior of nanoparticles on surfaces can be offered. "Configurational diagram", showing the final position of the particle as a function of its height and diameter was constructed.

## Grain Boundary Diffusion in C<sub>60</sub> Thin Films

E. Katz<sup>1</sup>, S. M. Tuladhar<sup>1</sup>, A.I. Shames,<sup>2</sup> S. Shtutina,<sup>2</sup> and D. Faiman<sup>1,2</sup>

<sup>1</sup>*Department of Solar Energy and Environmental Physics, Blaustein Institute for Desert Research, Ben-Gurion University, Sede Boqer Campus, Israel*

<sup>2</sup>*Department of Physics, Ben-Gurion University, Beersheba, Israel*

The most commonly practiced kind of doping of C<sub>60</sub> crystals is intercalation whereby dopants are located between the C<sub>60</sub> molecules in the interstitial positions of the host crystal structure. Intercalated fullerides may be produced by the simultaneous evaporation of C<sub>60</sub> molecules and dopant atoms or by diffusion of dopant atoms into pristine C<sub>60</sub> crystal. The latter may occur as a spontaneous process or it can be induced by an external stimulus, like vapor pressure or an electric field applied to the sample.

This paper focuses on the effect of grain boundaries on the diffusion processes in polycrystalline C<sub>60</sub> thin films. Electron Paramagnetic Resonance (EPR) spectroscopy was used to study diffusion of oxygen. Electrically induced diffusion of Au was investigated by *in situ* measurements of the film conductivity.

*Grain boundary diffusion of oxygen into C<sub>60</sub> films.*

Time-development of EPR signals ( $g = 2.0026 \pm 0.0002$ ) from C<sub>60</sub> films with various crystalline structure under air/light exposure is reported to consist of two clearly distinguished regions of fast and slow growth. Improvement of the film structure, and in particular increase in grain size, leads to a deceleration of the “fast” growth. The results are explained assuming that EPR signal growth is controlled by oxygen diffusion, along grain boundaries and into grains, during the “fast” and “slow” periods, respectively. Fast decrease of the EPR signal as a result of *in situ* pumping strongly supports this model.

*Diffusion of Au into C<sub>60</sub> films under the action of an external electric bias.*

We report the effect of the external electric field on the *in situ* measured conductivity of C<sub>60</sub> films with different crystallinity. Semiconductor behavior with the increased conductivity values (by orders of magnitude) and decreased conductivity activation energies has been demonstrated for the doped samples. We observed a strong correlation of the rate of conductivity increase during the exposure with the crystalline structure of the films: the former decreased with an increase of the film grain sizes. Furthermore, we demonstrate the relationship between the decrease in activation energy and crystalline structure of the samples. The minimum value of activation energy after the exposure (i.e., the maximum doping effect) was observed for the samples with smallest grains. The maximum activation energy (i.e., the minimum doping effect) was observed for the sample with largest grains.

The results are explained by electrodiffusion of Au from an electrode, dominated by the grain boundary diffusion, and the subsequent intercalation of C<sub>60</sub> lattice by Au atoms.

## The Impact of Grain Boundary Diffusion on the Low Temperature Oxidation Mechanism in Nanocrystalline $\text{TiO}_{2-\delta}$ Thin Films

Avner Rothschild<sup>1</sup>, Yigal Komem<sup>1</sup>, and Frederic Cosandey<sup>2</sup>

<sup>1</sup> Faculty of Materials Engineering, Technion – Israel Institute of Technology, Haifa 32000, Israel.

<sup>2</sup> Department of Ceramics and Materials Engineering, Rutgers University, Piscataway, NJ 08854-8065, USA.

$\text{TiO}_2$  is an insulator at stoichiometric composition, but the reduced compound  $\text{TiO}_{2-\delta}$  is an  $n$ -type semiconductor due to oxygen vacancies serving as donors. The electrical conductivity ( $\sigma$ ) is proportional to the concentration of oxygen vacancies; therefore it is very sensitive to the oxygen deficiency ( $\delta$ ). Since the latter depends on the oxygen pressure ( $p_{\text{O}_2}$ ) in the ambient atmosphere,  $\sigma$  is a function of  $p_{\text{O}_2}$ . Therefore,  $\text{TiO}_2$  can be used for oxygen sensing.

At high temperatures ( $\geq 700^\circ\text{C}$ ) the redox reaction  $\text{TiO}_2 \rightleftharpoons \text{TiO}_{2-\delta} + \frac{\delta}{2} \text{O}_{2(\text{gas})}$  is very fast due to the high chemical diffusivity at these temperatures. The chemical diffusivity diminishes with decreasing temperatures according to Arrhenius law, with an activation energy of  $0.6 \div 0.8$  eV. Therefore, at low temperatures ( $\leq 400^\circ\text{C}$ ) the redox reaction becomes too sluggish to cause any significant effect on the electrical properties of bulk  $\text{TiO}_2$  (during a reasonable measurement period). However, in *nanocrystalline*  $\text{TiO}_2$  this reaction could be greatly enhanced by grain boundary diffusion, with the effective diffusion distance being reduced to half the grain size. Consequently, its influence on the electrical properties could be significant even at relatively low temperatures. This unusual phenomenon is the focus of this paper.

In the first part of this paper we present a phenomenological model for the low temperature oxidation mechanism in nanocrystalline  $\text{TiO}_{2-\delta}$  films, and derive equations describing the oxidation kinetics and the resultant change in the electrical conductance as a function of time. In order to account for the effect of grain boundary diffusion, the usual parabolic law of oxidation,  $X = (K_p t)^{1/2}$ , is replaced by a modified parabolic law,  $X = \{2K_p [t + C(1 - e^{-\beta t})]\}^{1/2}$ , where  $X$  is the thickness of the oxidized layer,  $K_p$  is the parabolic rate constant,  $t$  is the elapsed time since the onset of oxidation, and  $C$  and  $\beta$  are phenomenological constants. Using this modified parabolic law we derive an expression describing the change in the electrical conductance as a function of time during the oxidation process.

In the second part of the paper we compare the expected oxidation behavior with experimental results from  $\text{TiO}_2$  thin films (100-200 nm) with a typical grain size of 50 nm that were exposed to a constant oxygen pressure of 0.65 Pa after being equilibrated at a vacuum of 0.008 Pa. The electrical conductance was measured during these experiments, which were done at various temperatures between 100 and  $325^\circ\text{C}$ . This comparison yields an excellent fitting, from which a value of  $0.69 \pm 0.02$  eV could be deduced for the activation energy for chemical diffusion in the  $\text{TiO}_2$  grains.

## **Wetting and Wetting Transitions in Fluids and Solids**

John W. Cahn,

*Materials Science and Engineering Laboratory, NIST, Gaithersburg MD, USA*

Surfaces, including grain boundaries, interfaces, etc. are areas of contact between phases or grains. When a surface is perfectly wet by another phase, the direct contact between the original phases is removed from the microstructure and replaced by a layer of a "wetting" phase (which can be solid). The onset of such perfect wetting is a transition that displays many of the features of ordinary phase transitions, and can be depicted on phase diagrams. Many other surface phase transitions have been found to result from surface anisotropy. Because a wetting transition is almost universally expected in fluid (but not solid) systems with critical points, critical point systems have received much attention.

The behavior of junctions of surfaces in multiphase fluid systems is examined in the vicinity of a perfect wetting transition. It is found that well before the conditions are reached where a surface disappears everywhere, it disappears at all the higher junctions involving that surface, creating other junctions involving the wetting phase. Unusual multiphase junctions, such as line junction of more than three phases, and point junctions of more than four phases can occur in equilibrium as a result. Unlike line triple junctions in which the equilibrium dihedral angles are fixed and determined by a balance of surface tension forces, the force balance for line quadrijunctions permits a range of angles. There is qualitative agreement with experiments for this in a number of systems. These relatively simple wetting phenomena in fluids have to be modified for the anisotropy of solid surfaces, their structures and the elastic effects generated.

## **Alternative Pathway of Dewetting at the Liquid/Liquid Interface**

Rachel Yerushalmi-Rozen<sup>1</sup>, Tobias Kerle<sup>2,3</sup>, and Jacob Klein<sup>2</sup>

<sup>1</sup>*Department of Chemical Engineering, Ben Gurion University in the Negev, 84105 Beer Sheva, Israel,* <sup>2</sup>*Department of Materials and Interfaces, Weizmann Institute of Science, 76100 Rehovot, Israel,* <sup>3</sup>*Current address: Silvio O. Conte National Center on Polymer Research, University of Massachusetts, Amherst, MA 01003, USA*

Experimental observations of a non-classical pathway of dewetting which takes place in thin films of partially miscible liquid mixtures is described. The process is associated with the evolution of a directed dewetting front at the newly formed interface between two coexisting liquid phases. As the dewetting front advances from the sample edges inward, it results in film rupture at rates much faster than allowed by classical mechanisms. We suggest that a Marangoni flow is responsible for the initiation of the dewetting front, and that coupling between the two layers enables the process. The alternative, more rapid, pathway to the known processes of dewetting may be responsible for fast distraction of thin liquid films which contain more than a single component.

## **Design Strategy of Multi-Functional Biological Materials**

Weiner Steve, Addadi Lia and Wagner H. Daniel\*

*Departments of Structural Biology, and Materials and Interfaces\*, Weizmann Institute of Science, Rehovot, Israel 76100*

Some of the mineralized materials that organisms produce have multipurpose functions; the “concretes” of the biological world. These materials are different in structure and composition, yet they all have a similar overall design strategy, namely to be as isotropic as possible.

The optimal isotropic materials are those with so-called amorphous structures. Many organisms do use amorphous silica for structural purposes. Most of the siliceous skeletons formed are micron sized, presumably to minimize the chance of failure by cracking. Amorphous calcium carbonate is also proving to be a relatively widely used isotropic material, despite the fact that it is inherently unstable.

The echinoderms (sea urchins, sea stars etc.) have skeletons composed of 99.9% calcite and 0.1% organic macromolecules. Each skeletal element, which may be up to tens of centimeters long, is a single crystal. These crystals cleave with a conchoidal fracture even though calcite has well developed cleavage planes. The conchoidal fracture properties are due to proteins occluded inside the crystal on planes oblique to the cleavage planes. So although the material structure remains highly anisotropic, the molecular scale design strategy essentially results in it behaving mechanically as if it is isotropic.

The crossed lamellar structure of mollusk shells is composed of elongated rod-shaped crystals of aragonite packed into arrays that are rotated relative to each other at different hierarchical levels. Its elastic mechanical properties are significantly more isotropic than individual aragonite crystals, due to this sophisticated packing strategy.

The major all-purpose material of vertebrates is lamellar bone. Its building block, the mineralized collagen fibril, is highly anisotropic. Some members of the bone family of materials are composed of parallel arrays of mineralized collagen fibrils, and their elastic modulus anisotropy ratio is around 2.4. Multipurpose lamellar bone, however has an anisotropy ratio of around 1.6. This is attributed to its unique rotated plywood structure. Even more impressive is dentin, another member of the family of bone materials. Measurements of microhardness in three orthogonal directions reveal almost no differences, making this material essentially isotropic. This is ascribed to the almost random orientations of the mineralized fibrils in one plane, combined with the lack of preferred orientation of the crystal layers even between neighbouring fibrils.

The overall design strategy of multi-purpose biological materials is therefore to be as isotropic as possible. The diverse ways in which this is achieved may provide materials scientists with novel ideas for improving the properties of synthetically produced materials.

## **Energetics and Kinetics of Surfaces and Interfaces in Fe-Pb System**

Jean-Philippe Monchoux, Elazar Y. Gutmanas, and Eugen Rabkin

*Department of Materials Engineering, Technion, Haifa, Israel.*

The physics of the interaction between solid Fe and liquid Pb is of great importance from a technological point of view since in the accelerator-driven systems (ADS) these two materials will serve in contact with each other under high temperature and irradiation doses. The behavior of this solid-liquid couple, largely unknown, has then to be accurately studied in order to ensure safety of the device.

Though steel and (Pb-Bi) are planned to be used in the final ADS assembly, we used pure Fe and Pb in our experiments in order to avoid complicated chemical effects. Our goal is to study the phenomena occurring at the solid-liquid interface during surface and grain boundary wetting experiments.

To achieve a good physical contact between Fe and Pb, a new method of depositing Pb droplets has been developed, based on powder metallurgy technique. Fe-5wt.%Pb alloys with homogeneously distributed Pb particles of 5  $\mu\text{m}$  size have been firstly prepared. Then the samples were annealed in the temperature range 650-850° C in a flow of  $\text{H}_2$ . Due to volume expansion during melting, liquid Pb is in a high compressive state inside the material and tends to reach the sample surface. It forms there droplets of 10 to 100  $\mu\text{m}$  in diameter. Then, by evaporation of the droplets, the solid-liquid interface is revealed and studied by AFM.

For three kinds of interfaces (Fe-liquid Pb, Fe-Pb vapor, Fe- $\text{H}_2$ ) grain boundary grooves are formed on the samples surface during annealing. These grooves are characterized by their width  $w$ , from which the matter transport mechanism and its kinetics can be obtained, and by the dihedral angle  $\theta$  at the tip of the groove, giving the ratio of the interfacial and grain boundary energy.

It has been shown that  $\theta$  was large (120-140°), thus indicating that the wetting of grain boundaries in  $\alpha$ -Fe by liquid Pb is imperfect. Furthermore the effect of the ferromagnetic-paramagnetic transformation on the surface diffusion coefficient of Fe has been revealed. Under liquid Pb the matter transport mechanism has been determined as bulk diffusion of Fe atoms in the liquid, but for temperatures lower than 675° C this mechanism changes to interfacial diffusion, resulting in a drop of the diffusivity by 3 to 4 orders of magnitude. The reason of such a sudden change of diffusivity may arise from the formation of an oxide or segregation layer on the sample surface.

## **Atomistic Study of Structural Correlations at a Model Liquid-Solid Interface**

Adham Hashibon<sup>1</sup>, Joan Adler<sup>1</sup>, Michael W. Finnis<sup>2</sup>, and Wayne D. Kaplan<sup>3</sup>

<sup>1</sup>*Department of Physics, Technion, Haifa, Israel.*

<sup>2</sup>*Atomistic Simulation Group, School of Mathematics and Physics,  
The Queens University of Belfast, Belfast BT7 1NN.*

<sup>3</sup>*Department of Materials Engineering, Technion, Haifa, Israel.*

Metal-ceramic interfaces play a prominent role in a variety of technological applications that range from electronic devices to protective coatings and high-temperature structural components. The functionality of these systems depends crucially on their macroscopic properties such as fracture, yield, and electrical conductivity. These properties are strongly correlated with microscopic details of the metal-ceramic interface, such as bonding, chemistry, diffusion, and structure. Correlating macroscopic properties to the structure and chemistry of interfaces is one of the most intriguing topics in materials science.

Atomistic simulations, such as Molecular Dynamics or Monte Carlo permit the controlled study of these systems at the atomistic level for a large number of atoms and for large structures. However, the main limitation to such simulations is the lack of appropriate interatomic potential schemes which can model both metallic and ionic bonding across the interface. Nevertheless, simplified models can be used to obtain basic qualitative insights into the problem.

In this study we explore structural correlations at a metal-ceramic interface with Molecular Dynamics simulations of a model aluminium system with the Ercolessi-Adams potential and up to 4320 atoms. Several rows of substrate atoms are pinned to equilibrium crystalline positions to mimic a rigid ceramic substrate, and the remaining aluminium atoms form a liquid metal whose atoms are free to move. The density profile and inplane structure at the interface are investigated for different interface crystallographic orientations and temperatures. An exponential decay of the density profile was observed,  $\rho(z) \approx \exp(-\kappa z)$ , leading to the definition of  $\kappa$  as a quantitative measure of the ordering at the liquid-solid interface. We find a direct correlation between the amount of ordering in the liquid phase and the underlying substrate structure.

## **About the Importance of Nanometer-Thick Intergranular Penetration in the Analysis of the Liquid Metal Embrittlement Mechanisms**

K. Wolski, N. Marié, V. Laporte, M. Biscondi

*Centre SMS/MPI, Ecole des Mines de St-Etienne, CNRS URA PECM  
158, cours Fauriel 42 023 Saint Etienne FRANCE*

Liquid Metal Embrittlement (LME) is a mode of very rapid intergranular fracture which requires simultaneous action of stress and liquid metal on another solid metal. It occurs above the so called wetting transition temperature i.e. at temperatures where grain boundary wetting and penetration take place. The recent interest in LME is due to the development of the accelerator driven nuclear waste incinerator in which structural materials have to be capable of long operation under contact with liquid metal.

The purpose of this presentation is (i) to show the evidence for the nanometer-thick intergranular penetration (IGP), which does occur in at least two model systems and results in a strong embrittlement of grain boundaries (ii) to suggest a general procedure to check whether nanometer-thick IGP has occurred or not and (iii) to discuss the importance of the nanometer-thick films in the analysis of the LME mechanisms.

First, the evidence for the nanometer-thick IGP will be given in two model systems : Ni-Bi [1] and Cu-Bi [2], which were chosen for the experimental investigation because of their good wettability, rapid intergranular penetration and room temperature brittleness. It will be shown that in both systems liquid Bi-rich alloy quickly penetrates through grain boundaries and results in the formation of a long nanometer-thick films, which are too thin to be detected by SEM but lead to the strong IG brittleness [3]. The thickness of these films were determined by Auger Electron Spectroscopy (AES) after "in situ" fracture within main Auger chamber. Quantification based on internal bicomponent standards confirms the formation of some nanometer thick films rather than bismuth segregation [4].

Then, the necessity for a low temperature mechanical testing to reveal the total depth of intergranular penetration will be underlined. In Cu-Bi system, the analysis of the non-zero dihedral angles, on transverse polished sections, doesn't suggest any IGP. In Ni-Bi system, the grooves develop the "finger-like" shape and extend to the micrometer-thick films and once again there are no features indicating any IGP ahead of the micrometer-thick film tips. In both cases, those optically or SEM visible features are much shorter than the length of intergranular embrittlement. Assuming that this penetration results in a room temperature brittleness or in the case of intrinsical GB brittleness of solid metal (W, Mo), a general procedure based on room temperature bending or tensile tests and AES observations will be outlined and applied to the W/Pb system.

Finally, the implication of these nanometer-thick films on the LME mechanisms will be discussed. As LME requires simultaneous action of intergranular penetration and stress it can only occur at high temperature where intergranular films are at the liquid state. As liquids, they can hardly withstand any applied stress but in the same time can accelerate the crack advance rate at the tip of the liquid film. Consequently, it is postulated that the mechanisms of LME should be analysed with respect to the nanometer-thick film tip.

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## **Wetting in Multiphase Systems with Complex Geometries**

Dominique Chatain<sup>1</sup>, Paul Wynblatt<sup>2</sup>, Serge Hagège<sup>3</sup>, Ellen J. Siem<sup>4</sup>, and Craig Carter<sup>4</sup>

<sup>1</sup>*Centre de Recherche sur les Mécanismes de la Croissance Cristalline-CNRS, Marseille, France.*

<sup>2</sup>*Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, USA.*

<sup>3</sup>*Centre d'Etudes et de Chimie Métallurgiques-CNRS, Vitry-sur-Seine, France.*

<sup>4</sup>*Department of Materials Science and Engineering-MIT, Cambridge, USA.*

We address the effects of varying wetting conditions on the shapes and distribution of confined two-phase systems. The wealth of configurations obtained for embedded two-phase particles, solid/fluid or fluid/fluid, within a solid cavity is presented. This work could be helpful in the study of nano-embedded particles.

## **Reactive Solid State Dewetting: Cavity Nucleation in the System Ag-Ni-O**

H. de Monestrol, L. Schmirgeld-Mignot, S. Poissonnet, Ch. Lebourgeois and G. Martin

*Service de Recherches de Métallurgie Physique, DEN, CEA Saclay, 91191 Gif sur Yvette,  
France*

Micrometric silver films vapour deposited onto high purity nickel substrates (single or polycrystalline) dewet the substrate after an annealing at high temperature in an oxygen atmosphere while the films remain stable after an annealing at the same temperature in a nitrogen atmosphere. Dewetting occurs when a nickel oxide layer is formed at the silver-nickel interface as a consequence of oxygen diffusion through the silver film.

Scanning Electron Microscopy (SEM) of cross-sections reveal that one of the main mechanisms of dewetting is the nucleation of cavities at the Ag-NiO interface which grow towards the free surface of the Ag film. They are formed at grain boundaries and triple junctions but also in the core of Ag grains. Such cavities should be unstable from a thermodynamic point of view and we propose a simple model explaining their growth because of a vacancy supersaturation at the Ag-NiO interface which is driven by the oxidation process.

The influence on dewetting of different parameters such as annealing temperature (in the range 923-1123K), time (10 minutes to 8 hours), partial oxygen pressure (from  $6 \times 10^{-4}$  to 84 mbar) and thickness of the film (0.5 to 2  $\mu\text{m}$ ) has been determined.

## **Intergranular Melting of Nanocrystalline Nd<sub>2</sub>Fe<sub>14</sub>B Studied by Means of Radiotracer Diffusion**

Martin Eggersmann<sup>1</sup>, Feng Ye<sup>1</sup>, Oliver Gutfleisch<sup>2</sup>, and Roland Würschum<sup>1,3</sup>

<sup>1</sup> *Forschungszentrum Karlsruhe, Institut für Nanotechnologie, Karlsruhe, Germany*

<sup>2</sup> *Institut für Festkörper- und Werkstofforschung Dresden, Germany*

<sup>3</sup> *Institut für Technische Physik, TU Graz, Austria*

Despite the great technical relevance of Nd<sub>2</sub>Fe<sub>14</sub>B as the permanent magnet material with the highest energy density, no data on the self-diffusion in this system are available. This is remarkable in view of the fact that diffusion, in particular, in the intergranular liquid films formed in Nd-rich alloys at high temperatures, is of great importance for the metallurgical processing of these materials.

The present work aims at grain-boundary (GB) diffusion studies in Nd<sub>2</sub>Fe<sub>14</sub>B below and above the intergranular melting transition ( $T \sim 675^\circ\text{C}$ ) using the radiotracer technique with the isotope <sup>59</sup>Fe. A preliminary evaluation of the diffusion profiles on the basis of grain-boundary diffusion kinetics of type B yields the product  $D_{\text{GB}}\delta = 2.7 \times 10^{-11} \exp(1.8 \text{ eV/kT}) \text{ m}^3\text{s}^{-1}$  of the grain boundary diffusivity  $D_{\text{GB}}$  and thickness  $\delta$  in the solid phase assuming a volume self-diffusivity as in  $\alpha$ -Fe.

Above the intergranular melting transition a substantial increase of  $D_{\text{GB}}\delta$  could be observed. The intergranular melting process is discussed in view of the fact that no abrupt increase of  $D_{\text{GB}}\delta$  occurs. The influence of intergranular alloying with Co is addressed.

## **Possibilities of Synchrotron Radiation Imaging Techniques for the Study of Grain Boundary Related Phenomena**

W. Ludwig<sup>1</sup>, D. Bellet<sup>2</sup>, S.F. Faester<sup>3</sup>, H.F. Poulsen<sup>3</sup>, J. Susini<sup>1</sup>

*1 European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France*

*2 Lab. GPM2, INPG, BP 46, 38 402 St-Martin-d'Hères, France*

*3 Risoe Nat. Laboratory, Roskilde, Denmark*

Modern synchrotron radiation X-ray imaging techniques open interesting new possibilities to study phenomena like grain boundary wetting, grain growth, electromigration, etc. The aim of this contribution is to draw a picture of the state of the art and to encourage future research activities using this new characterization tools.

After a short introduction to relevant synchrotron radiation imaging techniques like X-ray microscopy, micro-radiography, micro-tomography and a novel 3D diffraction technique we will illustrate the potential of these techniques with the help of selected examples related to grain boundaries:

- In-situ observation of the penetration of liquid Ga along Al grain boundaries by means of X-ray micro-radiography.
- Characterization of wetting layers in the bulk of polycrystalline Al samples by X-ray micro-tomography and 3D grain orientation imaging (X-ray tracking technique).
- Visualization of the 3D grain structure in Al alloys using the Ga decoration technique.
- In-situ observation of electro-migration using full-field X-ray microscopy.
- In-situ observation of grain growth using new 3D imaging techniques.

We will finally discuss the potential of X-ray micro-fluorescence to improve the detectability of nanometric grain boundary wetting layers and present first in-situ observations of grain boundary penetration by microscopic liquid films in high temperature systems like Al-Sn, using a specially designed furnace, compatible to the requirements of tomographic imaging.

## **On the Correlation of Grain Boundary Segregation in Intermetallics**

Pavel Lejcek<sup>1</sup>, and Anna Fraczkiewicz<sup>2</sup>

<sup>1</sup>*Institute of Physics, AS CR, Praha, Czech Republic*

<sup>2</sup>*Ecole Nationale Supérieure des Mines, St. Etienne, France*

It is generally accepted that presence of boron in ordered intermetallic alloys such as Ni<sub>3</sub>Al, NiAl and FeAl, enhances their ductility. It is proved that in these materials, boron segregates at grain boundaries and forms directed bonds with the matrix atoms parallel to the boundary plane [1,2]. The experimental studies of grain boundary segregation in intermetallics suggest, however, that grain boundary saturation occurs despite of the bulk content of boron. Recently, a concentration dependence of equilibrium boron segregation at grain boundaries of polycrystalline Fe-40at.%Al base intermetallics was measured at 400°C [3]. In this study, the saturation of grain boundaries at the level of about 13 at.% of boron was also reported corresponding to the bulk content of this segregant of 800–2000 at.ppm that is beyond the limit of its solid solubility in this material.

In the present contribution, two methods of correlation of experimental data on grain boundary segregation of boron in intermetallics are compared: the Fowler segregation isotherm and the Langmuir–McLean isotherm considering reduced number of grain boundary positions available for segregation [4]. It is shown that the latter approach provides physically acceptable results and the limited number of segregation positions can be explained by a high degree of the order of the system. A comparable correlation according to the Fowler isotherm requires large positive interaction parameter suggesting strong repulsion of boron atoms which seems to be physically improbable. The capability of both types of correlation is documented on recent experimental data on boron segregation at grain boundaries in FeAl and Ni<sub>3</sub>Al base intermetallics.

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## **Continuum Theory of Interfacial Segregation**

A. Umantsev

*Department of Materials Science and Engineering, Northwestern University,  
Evanston, IL 60208.*

Theoretical work in the field of interfacial segregation is mainly focused on the Gibbsian approach that uses the dividing surface construct. The purpose of this presentation is to discuss a consistent continuum approach to the problem of equilibrium interfacial segregation. At first I will describe the application of continuum methods to the problem of interfacial structure. To account for possible symmetry changes in the system we use a Landau expansion of the coarse-grained free energy, which requires introduction of order parameters. There is a particular benefit in using a continuum approach for coherent systems, because the continuity of strain across the interface warrants the coherency without any additional constraints.

Then I will derive the Gibbs adsorption theorem in the framework of a continuum approach and compare the results with that of the dividing surface construct. The segregation at homophase and heterophase interfaces that appear as a result of polymorphous, solid-liquid or ordering transformations in multicomponent alloys will be considered on the common grounds. The continuum method allows one to find the entire distribution of segregating species near an interface, which may be compared with experimental observations. The interfacial segregation is calculated for the case of a linear thermodynamic system where it is found to vanish at a heterophase interface and have the critical dependence on temperature and composition at a homophase interface. The physical driving force for the interfacial segregation will be discussed.

## **Atomic-Scale Structure and Chemistry of Segregation at Heterophase Interfaces\***

Dieter Isheim and David N. Seidman

*Department of Materials Science and Engineering, Northwestern University, 2225 N. Campus Drive, Evanston, IL 60208-3108*

The structure and local chemistry of internal interfaces in multiphase alloys is a key issue for understanding many scientific phenomena and technological problems. The interrelationships between interfacial structure and solute segregation has been explored for grain boundaries (homophase interfaces) both by computer simulations and experiments, for example, see [1]. There is, however, a lack of experimental data and modeling for *heterophase* interfaces. This study is an experimental investigation exploring segregation at coherent and semicoherent heterophase interfaces.

Fe- 2 at.% Mo-X alloys, where X = 0.5 at.% Sn or 0.4 at.% Sb, are internally nitrided by annealing in an ammonia atmosphere. Nitridation at 550°C produces a dispersion of small coherent plate-shaped precipitates at a high number density. Nitridation at 600°C generates a duplex-type precipitate microstructure containing coarse semicoherent precipitates, in addition to a structure of smaller platelets similar to those formed at 550°C.

Atom-probe analyses show that segregation of Sn or Sb is small or nonexistent at the broad interfaces of the coherent precipitates formed at 550°C. On the other hand, segregation of up to 7 atoms nm<sup>-2</sup> is detected at the interfaces of coarse molybdenum nitride precipitates formed at 600°C. These precipitates have a well defined network of misfit dislocation as detected by weak-beam dark-field imaging techniques, whereas HREM shows that the small precipitates formed at both nitridation temperatures are either fully coherent or have many fewer dislocations than is geometrically necessary to accommodate the misfit strain. An appreciable level of segregation of Sn and Sb is related to the presence of the misfit dislocations, whose cores and localized strain fields provide attractive sites for the oversized Sb or Sn atoms. Our research shows, for the first time, the importance of misfit dislocations on solute segregation at heterophase interfaces.

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## **Grain Boundary Dynamics: a Novel Tool for Microstructural Control**

G. Gottstein<sup>1</sup>, D.A. Molodov<sup>1</sup>, M. Winning<sup>1</sup>, L.S. Shvindlerman<sup>1,2</sup>

<sup>1</sup>*Institut für Metallkunde und Metallphysik, RWTH Aachen, 52056 Aachen, Germany*

<sup>2</sup>*Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka,  
Moscow distr. 142432, Russia*

The microstructural restoration phenomena recrystallization and grain growth are processes with major impact on microstructure development and thus material properties. Grain boundary migration is the key mechanism of these processes, and microstructure evolution can be biased at desire if grain motion can be effectively influenced. We will present evidence that it is possible to affect the motion of grain boundaries by a variety of externally controlled driving forces. Albeit small these effects cause major and adjustable changes of boundary motion. Besides the well known chemical effects like impurity drag the coupling of boundary migration with magnetic and elastic fields will be addressed. Moreover, we will discuss the role of processing parameters like temperature or pressure on mechanism selection. Special attention will be given to the role of dislocation-boundary interaction which is a key issue in recrystallization. Finally, the consequences of boundary connectivity in terms of grain boundary networks with triple lines and quadruple junctions will be taken into account.

## **Interface Controlled Plasticity in Thin Metal Films**

Gerhard Dehm<sup>1</sup>, T. John Balk<sup>1</sup>, Beverley J. Inkson<sup>2</sup>, Thomas Wagner<sup>1</sup>, and Eduard Arzt<sup>1</sup>

*(1)Max-Planck-Institut für Metallforschung, Seestr., Stuttgart, Germany*

*(2)Department of Materials, Oxford University, Parks Road, Oxford, U.K.*

Thin metal films with thickness in the sub-micrometer range are frequently used in semiconductor devices and in micro-systems. During processing the metal layer is subjected to temperature cycles, which result in thermal stresses that can significantly exceed flow stresses in the corresponding bulk metal. Furthermore, the flow stresses of thin metal films constraint by a substrate increase with decreasing film thickness, which can affect the reliability of small-scale devices. The high flow stresses of thin metal films are explained to be a result of the dimensional constraint on lattice dislocations, which begin to notice the presence of interfaces, surfaces and for polycrystalline films also grain boundaries. Assuming that a dislocation advancing through a metal film leaves behind a dislocation segment at the film/substrate interface Nix [1] calculated an increase in flow stress with decreasing film thickness. However, flow stresses in thin Cu films grown with a columnar microstructure on diffusion-barrier coated Si substrates exceed the flow stresses predicted by this model. The reason for this discrepancy is not yet understood.

In the present study, plan-view and cross-sectional transmission electron microscopy (TEM) specimens of thin metal films on substrates were thermally cycled *in-situ* in a TEM in order to analyze dislocation-based plasticity and dislocation-interface interactions. The experiments revealed that dislocation motion is influenced by the structure of the film/substrate interface. For Cu and Al films grown on silicon wafers coated with *amorphous* diffusion barriers, the TEM studies indicated that dislocations are pulled towards the interface, where their contrast finally disappears. However, for Al films deposited on Al<sub>2</sub>O<sub>3</sub>-substrates, threading dislocations advance through the layer and drag behind interfacial dislocation segments. In this case, the interface is between two *crystalline* lattices.

Furthermore, the *in-situ* TEM experiments were correlated with the mechanical properties of the Cu and Al films, which were measured by the substrate-curvature method using a laser scanning technique during thermal cycling. The *in-situ* TEM studies revealed continuous dislocation glide at elevated temperatures, while jerky dislocation motion occurred at low homologous temperatures. Since dislocation density remained nearly constant at values of  $\sim 3 \cdot 10^9 \text{cm}^{-2}$  to  $\sim 6 \cdot 10^9 \text{cm}^{-2}$ , independent of the film stress, it is assumed that the decrease in available thermal energy with decreasing temperature impedes dislocation motion and thereby contributes to the high flow stresses of the thin metal films.

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## **Nucleation of Recrystallization: A Vertex Dynamics Approach**

D. Weygand<sup>1</sup>, J. Lépinoux<sup>2</sup>, Y. Bréchet<sup>2</sup>

<sup>1</sup> *University of Groningen/NIMR, Department of Applied Physics, Micromechanics of Materials Group, Nijenborgh 4, 9747 AC Groningen, The Netherlands*

<sup>2</sup> *LTPCM/ENSEEG/INP de Grenoble, (UMR CNRS 5614), BP 75, 38402 Saint Martin d'Heres CEDEX, France*

The control of the grain microstructure obtained after heat treatment of the highly deformed metal is crucial for the performance of the material. The modeling of the evolution of the microstructure during the annealing process is done using the vertex dynamics method in two dimensions [1] initially developed for grain growth and extended to questions of recrystallization [2].

During the annealing process of a deformed metal, recrystallization occurs. Nucleation of the recrystallization is still a matter of discussion [3]. The bulging of grain boundaries has been proposed as a possible mechanism for nucleation of recrystallization by Bailey and Hirsch [4]. Bate and Hutchinson [5] have refined the "bulging mechanism", taking into account a subgrain structure on both sides of the bulging grain boundary. This idea is the starting point for this investigation.

A two dimensional description of the deformed microstructure is chosen. We assume that the total deformation energy of a grain is stored as subgrain interface energy. The driving force for the evolution of the microstructure is therefore the reduction of the total interface energy (grain and subgrain boundaries). The physical parameters available are the mobilities and energies of the (sub)grain interfaces and the crystallographic orientations of the grain-and subgrains. As a first step we abstract to a two level model where an interface is either a grain or a subgrain boundary. Subgrain and grain boundaries have quite different mobilities and energies [3]. The influence of the ratio of the grain to subgrain mobility and energy is studied. It is observed that bulging of grain boundaries occurs as a consequence of size fluctuation in the subgrain structure, leading to an "abnormal growth" of some subgrains. The distribution of these nucleation sites is stochastic and scales with the available grain boundary length, keeping the subgrain size constant.

A more complex starting configuration consists of a polycrystal. The polycrystal adds as additional features triple points formed by grain boundaries and net curvature of grain boundaries. Therefore more topological constraints to the microstructural evolution are present. In the polycrystal the mean grain size after completed recrystallization in dependence of the physical parameters (grain boundary energy and mobility) and the subgrain microstructure is of interest as well as the nucleation rate.

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## **Structure of Grain Boundaries and Mechanical Behaviour of Submicrocrystalline Aluminium Alloys**

N.K. Tsenev, A.M. Shammazov

*Ufa State Petroleum Technical University, 450062, Ufa, Kosmonavtov St., 1, Russia.*

The present work considers structure of grain boundaries in various submicrocrystalline Al alloys processed by severe plastic deformation techniques, namely, equal-channel angular (ECA) pressing and high pressure torsion (HPT), i.e. intense plastic straining under high applied pressure using the Bridgman anvil. Structure evolution of grain boundaries during heating and plastic deformation of these alloys was studied. Influence of grain boundary structure on mechanical behaviour of submicrocrystalline Al alloys at low and elevated temperatures was investigated.

Submicrocrystalline Al-3%Mg alloy was used as a pattern alloy where a strange behaviour during annealing was revealed. The annealing of the alloy led to high density dislocations inside grains. As a result, an increase in microhardness was observed. Auger spectroscopic analysis showed intense grain boundary diffusion of Mg atoms during annealing of the submicrocrystalline Al-3%Mg alloy. Reasons for the increase in lattice dislocation density during annealing of the alloy is discussed.

The results of mechanical behaviour of various industrial submicrocrystalline Al-based alloys at room and elevated temperatures according to their grain boundary structure are presented. Nature of processing high strength and high-strain-rate low temperature superplastic states is considered.

## **Structure Evolution and Diffusion During Interphase Boundary Sliding in Sn-Based Binary Eutectics**

Faina Muktepavela, Janis Maniks

*Institute of Solid State Physics University of Latvia, Riga, Latvia*

The aim of this paper is to study the role of interphase energy and mechanoactivation effect on peculiarities of interphase boundary sliding and accompanying processes.

Mechanical behaviour of interphase boundaries (IB), stability of defects and microstructure in heavily deformed binary eutectics (Al-Sn, Zn-Sn, Pb-Sn, Cd-Sn, Bi-Sn) have been investigated. For these eutectics interphase boundary sliding (IBS) is the main mechanism of plastic deformation at room temperature, but IB energies are significantly different. Experiments were carried out on the atomically-clean surfaces of alloys and on the bimetallic joints with clean interphase boundaries. Different schemes and regimes of deformation were used.

It has been shown, that IBS for eutectics with high IB energy (Al-Sn, Zn-Sn) occurs by the dislocation gliding, followed by a marked strengthening and accompanied by the formation of narrow stable IB cracks with sharp angles. Grain size is not changed significantly during deformation and after annealing.

For eutectics Pb-Sn, Bi-Sn, Cd-Sn with low IB energy IBS occurs by the viscous flow and is accompanied by matched diffusion along IB. The softening of IB is observed. Intensity of softening and development of diffusion depend on the extent of preliminary deformation and values of IB energy. Estimates for Pb-Sn and Bi-Sn eutectics show very high values of diffusion coefficient along IB that are typical for liquids. Formation of very fine grained and non-homogenous structure ( $d \approx 0,05-1 \mu\text{m}$ ) under heavy plastic deformation is observed. The formation of pores or cracks in this case is not observed. This could be explained by intensive development of the IB diffusion and diffusion-promoted dissolution-precipitation processes. This causes fast healing of cracks, pores and other defects. However, in the structure of Cd-Sn some round pores has been observed. For all eutectics with low IB energy the annealing leads to increase of strength of IB. Transition of IB into stable state is more prolonged than recrystallization processes in phases.

In summary, the differences in the mechanical behaviour of the IB of deformed eutectics are observed and the main role of IB energy in the stability of defects and development of accommodation processes has been shown.

## **Effects of Surface Anisotropy on Grain Boundary Grooving**

Eugen Rabkin and Leonid Klinger

*Department of Materials Engineering, Technion, Haifa, Israel*

We studied the thermal grooving of grain boundaries in the coarse-grained Ni-rich NiAl polycrystals with the strong (001) texture. The morphology of grain boundary grooves was investigated by the atomic force microscopy (AFM). The observed morphologies were strongly affected by the proximity of singular (001) plane to the original surface of the specimen. For example, the grooves with the flat walls exhibiting no measurable curvature and the grooves with the apparent negative, concave curvature at the groove root were observed. These shapes are in apparent contradiction with the classical theory of grain boundary grooving due to Mullins.

We developed a theory of grain boundary grooving for the case in which at least one of the groove walls exhibits the low-index singular surface orientations. We assumed that surface diffusion is a dominating transport mechanism and adopted a small-slope approximation. The results of calculations are in a good agreement with the experimental observations. Different types of groove morphologies were predicted. For some of them, the overall groove morphology for the case of very slow diffusivity along the singular surface is identical to the classical Mullins morphology, however, the value of dihedral angle at the groove root is different from the equilibrium value required by the Young equation. The implications of this finding for the experimental measurements of grain boundary energy are discussed.

Finally, the relative energies of the grain boundaries in NiAl were estimated from the experimental data and correlated with their misorientational degrees of freedom.

## **Correlation of Grain Boundary Character with Wetting Behaviour**

P. Wynblatt<sup>1</sup>, M. Takashima<sup>2</sup>, B.L. Adams<sup>3</sup> and A.D. Rollett<sup>1</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh  
PA, USA*

<sup>2</sup>*Kawasaki Steel Corporation, Kurashiki, Okayama, Japan*

<sup>3</sup>*Department of Mechanical Engineering, Brigham Young University, Provo UT, USA*

Wetting of 975 grain boundaries (GB's) by liquid Cu in an iron alloy has been studied as a function of the five macroscopic degrees of freedom (DoF's) of grain boundary character. In addition, a model of GB energy which accounts for the effects of all five DoF's has been developed. The experimentally observed wetting behavior will be interpreted in terms of the model, and it will be shown that reasonable overall agreement is obtained between experimental results and model predictions.

## Faceting of $\Sigma 3$ and $\Sigma 9$ Grain Boundaries in Copper

Boris B. Straumal<sup>1</sup>, Sergei A. Polyakov<sup>1,2</sup>,  
Ewald Bischoff<sup>2</sup>, Wolfgang Gust<sup>2</sup>, Eric J. Mittemeijer<sup>2</sup>

<sup>1</sup>*Institute of Solid State Physics, Russian Academy of Sciences,  
Chernogolovka, Moscow District, 142432 Russia*

<sup>2</sup>*Max-Planck-Institut für Metallforschung and Institut für Metallkunde,  
Seestr. 92, 70174 Stuttgart, Germany*

Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries (GBs). Faceting can be considered as a phase transition when the original surface or GB dissociates onto flat segments whose energy is less than that of the original surface or GB. GB faceting proceeds only close to the so-called coincidence misorientations. In this case the lattices of both grains form the coincidence site lattice (CSL) characterized by the parameter  $\Sigma$  (reverse density of coincidence sites). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. For the investigation of GB faceting a cylindric Cu bicrystal with an island grain was grown with the aid of the Bridgman technique from Cu of 99.999 wt.% purity. Grain 1 in this bicrystal is completely surrounded by grain 2 forming the  $\Sigma 9$   $\langle 110 \rangle$ -tilt GB. The  $\langle 110 \rangle$  axes in both grains are parallel to the growth axis. The faceting was analyzed in an *as-grown* bicrystal and after annealing at 1020, 800 and 600°C. It is well documented in the literature that close to the  $\{111\}/\{115\}$  inclination the  $\Sigma 9$  GB is unstable against the dissociation reaction:  $\Sigma 9 \rightarrow \Sigma 3 + \Sigma 3$ . This dissociation proceeds also in our case. The twins appear during the growth of the bicrystal instead of  $\{111\}_1/\{115\}_2$  or  $(110)\Sigma 9\text{CSL}$  facet. The profiles of the the formed GB thermal groove were analysed with the aid of atomic force microscopy. Wulff-Herring plots and GB phase diagrams have been constructed for the  $\Sigma 3$ ,  $\Sigma 9$  and  $\Sigma 9+\Sigma 3$  GBs. The energy of the symmetric  $\Sigma 3$  twin ( $\{111\}_1/\{111\}_2$  or  $(100)\Sigma 3\text{CSL}$  facet) is very low in case of exact coincidence. The second close packed plane ( $\{211\}_1/\{211\}_2$  or  $(010)\Sigma 3\text{CSL}$  facet) is the so-called asymmetric twin. The  $\{211\}_1/\{211\}_2$  facets are well documented for Al, Au,  $\text{AuCu}_3$  and Ge. However, the twin plates in Cu and Ag are not rectangular. The end facet form an angle of 82° with the  $\{111\}_1/\{111\}_2$  or  $(100)\Sigma 3\text{CSL}$  sides. Previous studies revealed that this 82° facet has a so-called 9R structure forming a plate of body-centred cubic GB phase in the face-centred cubic matrix. However, the analysis of the literature shows that the 82° facet appears only at high temperatures. At low temperatures the "normal" 90°  $(010)\Sigma 3\text{CSL}$  facets are present also in Cu. At 600°C the  $(110)\Sigma 3\text{CSL}$  facet appear in our samples. Therefore, the GB phase transitions occur between 0.95 and 0.64 of the absolute melting temperature.

## **On the Correlation between Grain Boundary Segregation, Faceting and Embrittlement in Bi doped Copper**

W. Sigle<sup>1</sup>, L.-S. Chang<sup>2</sup>, W. Gust<sup>1</sup> and M. Rühle<sup>1</sup>

<sup>1</sup>*Max-Planck-Institut für Metallforschung and Institut für Metallkunde, Stuttgart, Germany.*

<sup>2</sup>*National Chung-Hsing University, Department of Materials Engineering, Taichung, Taiwan.*

Copper bicrystals grown by the Bridgman technique have been doped with 25 and 65 at. ppm Bi, respectively. After annealing between 500 and 800°C the segregation was quantified using energy dispersive X-ray spectroscopy in a dedicated scanning transmission electron microscope. Grain boundary faceting on low-index planes was observed and the segregation level was significantly higher at the facets compared to the non-faceted segments. The fraction of faceted grain boundaries was found to increase with increasing annealing temperature implying that the faceting transition is thermally activated. Only the completely faceted grain boundary exhibits brittle behaviour. Faceting appears to be a necessary prerequisite for grain boundary embrittlement of the  $\Sigma 19a \{331\}$  grain boundary by the fact that it allows to incorporate enough Bi atoms. It is suggested that this embrittling mechanism may be a general phenomenon in Bi-doped Cu.

Faceted pores were observed in diffusion-bonded Cu(Bi) bicrystals. From the Wulff plot a surface energy anisotropy of 6 % is found at 600°C.

## **Effect of Diffusion Path on Electromigration-Induced Damage**

C.A. Volkert, J. Böhm, R. Mönig, J. Nucci, A. Straub, C. Witt, and E. Arzt

*Max Planck Institute for Metals Research, Seestraße 92, Stuttgart, Germany*

The passage of an electrical current through a metal segment leads to diffusive transport of the atoms from one end of the segment to the other. For the metals typically used in microelectronic circuits, such as Al and Cu, atoms are transported in the direction of the electron flow and accumulate at the anode end of the segment (positive terminal) and are depleted at the cathode end. The voids and hillocks that form can lead to electrical shorts and opens in device interconnects and therefore pose a serious reliability threat in the microelectronics industry, where large current densities are required to operate the devices.

Under typical testing conditions, electromigration in interconnects occurs along grain boundaries and interfaces, with occasional contributions from lattice diffusion. The dominant path for diffusion depends on the temperature, the interconnect microstructure, and the magnitude of the electric current. We have made use of in-situ SEM observations and various characterization techniques to try to determine which paths dominate for various samples and testing conditions and how the path influences the morphology of the damage that is formed. In particular, we have concentrated on hillock formation in polycrystalline and bamboo Al segments, void formation in damascene Cu segments, and  $\theta$  phase precipitation in Al-0.2%Cu segments. Examples will be given from these studies to illustrate how the details of the interfaces influence damage formation.

## Effect of Tracer Atoms on Grain Boundary Motion during Ag and Cu Grain Boundary Diffusion in Cu Polycrystals

Sergiy Divinski, Maik Lohmann, and Christian Herzig

*Institut für Materialphysik, Universität Münster,  
Wilhelm-Klemm-Straße 10, 48149 Münster, Germany*

Grain boundary (GB) diffusion measurements in polycrystals, where a part of the grain boundaries moves during the diffusion anneal, give a unique opportunity to study the GB motion in high-purity materials. In the present work the GB motion in Cu was investigated using the results of radiotracer GB diffusion measurements conducted on very pure Cu material (5N8 Cu) with tracers exhibiting fundamental differences in the solute-matrix atom interactions. The results on Ag (revealing a miscibility gap in the Ag-Cu phase diagram) [1] and Au (forming intermetallic compounds with Cu) [2] solute diffusion and on Cu self-diffusion [3] were analyzed.

The initial parts of the Ag and Cu penetration profiles turned out to be of sophisticated nature with a pronounced curvature in the coordinates  $\ln c$  vs.  $y^{6/5}$  (here  $c$  is the concentration and  $y$  the depth). Non-linear segregation effects can completely be ruled out for the case of Ag GB diffusion in Cu polycrystals due to the extremely small Ag tracer concentration in GBs in this case. Our estimations yielded e.g.  $c_{gb} \sim 10^{-4}$  (in atomic fractions) at penetration depths of about 10  $\mu\text{m}$ , where a pronounced curvature of the penetration profiles was observed and where direct volume diffusion of Ag is already negligible in the present experimental conditions.

These features are explained via the effect of GB motion during Ag GB penetration. The activation enthalpy of GB motion  $Q_{(\text{Ag})}^{\text{eff}}$  in this case was estimated to be  $Q_{(\text{Ag})}^{\text{eff}} \sim 95 \pm 10$  kJ/mol. This value is fairly close to the activation enthalpy of Cu GB self-diffusion,  $Q_{gb}^{\text{Cu}} = 72 \pm 2$  kJ/mol [3]. The GB penetration profiles of Cu self-diffusion in the same 5N8 Cu material [3] were re-analyzed accounting for the GB motion. The results of these two independent investigations with different tracers in the same high purity copper material are in good quantitative agreement. The absolute values of the GB velocity turned out to be somewhat smaller in the case of Cu self-diffusion and the effective activation enthalpy of GB motion  $Q_{(\text{Cu})}^{\text{eff}}$  in this case was  $Q_{(\text{Cu})}^{\text{eff}} \sim 103 \pm 12$  kJ/mol, a value which is only slightly larger than that for Ag GB diffusion in Cu. Tracer diffusion measurements of Au GB diffusion in Cu revealed practically no curvature of the experimental penetration profiles [2]. These results are discussed with respect to different solute-matrix atom interactions for the Ag-Cu and Au-Cu systems [4].

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## **On the Activation Energy of the Diffusion Process at Migrating Grain Boundaries**

Pawel Zieba<sup>1</sup> and Wolfgang Gust<sup>2</sup>

<sup>1</sup>*Institute of Metallurgy and Materials Science, Polish Academy of Sciences,  
Cracow, Poland*

<sup>2</sup>*Institut für Metallkunde der Universität Stuttgart, Germany*

Atomic transport along grain boundaries, being orders of magnitude faster than in the bulk, plays a key role in many technological processes. Therefore, the knowledge of the grain boundary diffusion characteristics is very useful for a proper design and a prediction of the behaviour of engineering materials.

Recently, analytical electron microscopy has shown to have a great potential in determining the grain boundary diffusion parameters for such systems as: Al-Zn, Ni-Sn, Co-Al and Cu-In. The obtained results confirmed that there are no significant differences in the values of the diffusivity,  $s\delta D_b$ , of stationary and migrating grain boundaries. Here,  $D_b$  is the grain boundary chemical diffusion coefficient,  $\delta$  is the grain boundary thickness, and  $s$  is the segregation factor. However, smaller attention was paid to the coincidence of the activation energies,  $Q_b$ , of both processes.

In the present paper, analytical electron microscopy was used, for the first time, for the determination of the  $s\delta D_b$  values of the migrating reaction front of the discontinuous precipitation reaction in a wide range of temperatures. In a consequence, it was possible to extract from the Arrhenius plot the values of the activation energy. From a comparison with the  $Q_b$  values for the Zn radiotracer diffusion in Al-Zn solid solutions it is concluded, that the energetic barrier, which has to be overcome in order to start the diffusion process, is the same for stationary and migrating grain boundaries.

## **Electromigration in Microelectronic Interconnects: Coupling Interface Electrotransport to Interface Reactions**

E. E. Glickman

*EE-Physical Electronics Dept., Tel Aviv University, Israel*

Electromigration (EM) in thin metal film interconnects is basically the problem of interface diffusion mass transfer (electrotransport) driven by electron wind. Important however is that the EM rate is not necessarily electrotransport controlled; in advanced interconnects, which are either short or separated into short polygranular segments, it can be controlled by the rate of atomic detachment /attachment processes ("interface reactions") which act at the conductor ends *in series* with electrotransport.

To reduce EM failures, the microscopic mechanisms of these reactions must be understood and their kinetics coupled to electrotransport.

In this lecture we review the topic from the perspective of our own contribution to the field, present the result of analytical and computer modeling, and compare them with the drift velocity EM kinetic data for Cu and Al interconnects. This enables to describe the mechanisms of the anode and cathode reactions, their effect on the total rate of EM, and understand how alloying elements can affect the EM rate through their influence on the reaction rates.

### Covered are the following issues:

1. Interface electrotransport: which are the major interfaces involved?
2. Grain boundary (GB) grooving as the cathode reaction: grooves as the carriers of EM displacement
3. Stress relaxation by GB diffusion creep as the anode reaction: creep controlled EM regime in short lines
4. Segregation effects in electrotransport, grooving, and creep in miniaturized interconnects.
5. Transition to reaction controlled regime in small dimension: a paradigm shift in the analysis of migration processes under potential fields (electric-, stress-, thermo-...) in microelectronic interconnects

## **Triple Junction Migration**

D. J. Srolovitz<sup>1</sup>, M. Upmanyu<sup>1</sup>, L. S. Shvindlerman<sup>2</sup>, G. Gottstein<sup>2</sup>

<sup>1</sup>*Princeton Materials Institute, Princeton University, Princeton, NJ 08540, USA.*

<sup>2</sup>*Institut für Metallkunde und Metallphysik, RWTH Aachen, D-52056 Aachen, Germany*

The motion of triple junctions is just as much an integral part of grain growth processes as grain boundary migration. In most grain growth theories, the triple junction is assumed to respond immediately to the motion of the grain boundaries such that they are in always in equilibrium with respect to the boundaries. In this paper, we will present the results of an extensive simulation study of the migration of grain boundaries with triple junctions. The simulations were performed using molecular dynamics. Results on the motion of triple junctions will be presented as a function of grain size, temperature, misorientation and direction of triple junction migration.

The main conclusion of the present study is that triple junction mobility is finite and can be sufficiently small to limit the rate of grain boundary migration. Triple junction drag is especially important at small grain sizes, low temperature and near high symmetry grain misorientations. Under these conditions, the triple junction angle  $\beta_d$  also shows substantial deviations from its equilibrium, static value,  $\beta_s$ .  $\beta_d$  can be either larger or smaller than  $\beta_s$ , depending on the tri-crystal geometry. Triple junction drag induces a dynamic force on the migrating triple junction that modifies the equilibrium Young-Duprè relation and thereby changes the triple junction angle.

The ratio of the triple junction to boundary mobility as represented by the parameter  $\Lambda$  shows an Arrhenius temperature dependence with two distinct regimes. A high temperature regime, where  $\Lambda$  is large and triple junction drag is insignificant and a low temperature regime where the opposite holds. Interestingly, it is in the low T limit that the activation energy (i.e., the slope of  $\ln\Lambda$  vs.  $1/T$ ) is much smaller than at high T. This is surprising because the activation energy for triple junction migration is larger than for grain boundaries. This effect can be understood in terms of the triple junction angle  $\beta_d$ . Similar results were obtained in recent experiments.

Another interesting feature of the present results is that the triple junction mobility depends upon the direction that the triple junction migrates. The difference in triple junction mobility can be as large as a factor of ten.

The implications of these results for grain boundary migration in polycrystalline and nanostructured materials will be discussed.

## **Triple Junction Motion in Metals**

L. S. Shvindlerman<sup>1,2</sup>, G. Gottstein<sup>1</sup>, D.A. Molodov<sup>1</sup>, V.G. Sursaeva<sup>2</sup>

<sup>1</sup>*Institut für Metallkunde und Metallphysik, RWTH Aachen, Kopernikusstr. 14,  
D-52056 Aachen, Germany*

<sup>2</sup>*Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka,  
Moscow Distr., 142432 Russia*

The motion of grain boundary systems with triple junctions and the interaction of these structural elements of a polycrystal are considered. The experimental results demonstrated that the motion of grain boundary systems with triple junctions can be controlled by slowly moving triple junctions. In a certain temperature interval these structural elements of a polycrystals can drag each other. The results of experiments dedicated to a direct comparison of a mobility of two types of grain boundary systems – with and without a triple junction – are considered and discussed. The experiments reveal a drastic difference between activation enthalpy of grain boundary and triple junction motion. The motion of the same triple junction in two direction was found to be essentially different as well. The process of grain growth in 2D systems is analyzed with respect to the controlling kinetics: from solely boundary kinetics, when grain growth in a polycrystal is determined by the Von Neumann-Mullins relation, to exclusively triple junction kinetics, when grain growth is governed by the mobility of triple junctions. It is shown that in the "intermediate" case, when the driving force for grain boundary motion and the characteristic mobility are grain boundary curvature and grain boundary mobility, respectively, a limited mobility of triple junctions essentially influences grain boundary motion. The Von Neumann-Mullins relation does not hold anymore, and this is the more pronounced the smaller the triple junction mobility. In case grain growth is determined by the mobility of grain boundary triple junctions (triple junction kinetics) all grains are transformed into regular polygons in the course of grain growth. The only exceptions are triangles: they collapse without transforming into a regular polygon. The respective relation for the rate of a change of grain area under triple junction kinetics is obtained and discussed with regard to microstructure evolution.

## **Effect of Dislocation Absorption on the Motion of Specific Grain Boundaries in Al-Bicrystals**

D. A. Molodov<sup>1</sup>, P. Konijnenberg<sup>1</sup>, W. Hu<sup>1</sup>, G. Gottstein<sup>1</sup>, L. S. Shvindlerman<sup>1,2</sup>

<sup>1</sup>*Institut für Metallkunde und Metallphysik, RWTH Aachen, Kopernikusstr. 14, D-52074 Aachen, Germany.*

<sup>2</sup>*Institute for Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow Distr., 142432 Russia*

The results of an investigation of grain boundary migration in slightly rolled (up to 1.3%) bicrystals of pure Al will be presented. In particular, the migration of  $\langle 111 \rangle$  pure tilt grain boundaries with rotation angles of  $38.2^\circ (\Sigma 7)$  and  $40.5^\circ$  was investigated. The motion of a  $40.5^\circ \langle 111 \rangle$  tilt boundary having an additional twist (component ranging between  $5.9^\circ$  and  $9.2^\circ$ ) was measured as well. The boundaries moved under the action of a constant capillary driving force provided by the grain boundary surface tension  $\sigma$  of the curved boundary,  $p = \sigma/a$ , where  $a$  is the width of the shrinking grain.

Experiments revealed that in the investigated range of deformation (up to 1.3%) the reduced grain boundary mobility  $A = v \cdot a = m \cdot \sigma$  ( $v$  - grain boundary migration rate,  $m$  - boundary mobility) for pure tilt boundaries substantially decreased with increasing deformation, i.e. increasing density of dislocations. The mobility effectively decreased for both investigated pure tilt boundaries due to a reduction of the preexponential mobility factor. The measured activation enthalpy for boundary migration in the framework of experimental error remain constant. The experiments also showed, however that for the non-tilt boundaries ( $40.5^\circ \langle 111 \rangle$  with additional twist components) there was practically no difference in the boundary mobility  $A$  in deformed and undeformed bicrystals.

Microstructural TEM investigations of rolled bicrystals containing a  $38^\circ \langle 111 \rangle$  boundary after its migration in deformed sample reveal the reason for this different behaviour. The pure tilt boundary was always observed to contain extrinsic dislocations, apparently swept by the boundary during its migration and not yet absorbed. The presence of these dislocations in the boundary appears to be the reason for a retardation of the boundary migration rate. If the dislocations are only adsorbed in the boundary without being decomposed or annihilated, their stress field - although certainly partly relaxed in the boundary - still contributes to the internal energy and is not released as driving force. In such case the boundary will not experience the full gain of stored dislocation energy, rather it has to drag along the swept dislocations, which degrade its mobility. Accordingly random boundaries are obviously more capable of absorbing (annihilating) the swept dislocations than special boundaries. In fact, TEM investigations have shown substantially fewer extrinsic dislocations in the random grain boundaries than in special boundaries. It is worthy to note that during TEM observations on random boundaries it was often seen that the dislocations moved affected by the electron beam. They moved forward the grain boundary and their contrast disappeared when they reached the boundary, obviously due to their annihilation in the boundary.

## **Simultaneous Grain Boundary Migration and Grain Rotation**

Moneesh Upmanyu<sup>1,2,3</sup>, David J Srolovitz<sup>2,3</sup>, W. C. Carter<sup>4</sup>, A. Lobovsky<sup>5</sup>, J. A. Warren<sup>5</sup>  
and Ryo Kobayashi<sup>6</sup>

<sup>1</sup>*Dept. of Materials Science & Eng., University of Michigan, Ann Arbor, MI USA;* <sup>2</sup>*Dept. of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ USA,*  
<sup>3</sup>*Princeton Materials Institute, Princeton, NJ USA,* <sup>4</sup>*Department of Materials Science and Engineering, MIT, Cambridge, MA USA,* <sup>5</sup>*Metallurgy Division, Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD USA,* <sup>6</sup>*Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan*

There are two distinct mechanisms by which grains can disappear during grain growth processes: namely, grain boundary migration and grain rotation. While the former is well known and clearly dominates at large grain sizes, there is an increasing body of evidence that suggests grain rotation may be important for small grain sizes. We perform atomistic and phase field simulations that demonstrate that both processes occur simultaneously in small grains. Molecular dynamics simulations of a shrinking grain embedded within a single crystal were performed in two-dimensions using empirical potentials over a range of misorientations (including both low sigma and irrational boundaries). Both grain size and grain orientations were monitored as a function of time. The simulations show that for the range of initial misorientations simulated, nearly all grains showed some degree of rotation while shrinking. In all cases, the grains rotated from their initial misorientation (between 30° and 50°) to a misorientations corresponding to low  $\Sigma$  misorientations, i.e.  $\Sigma 7$  (38°) and  $\Sigma 19$  (13°). While these misorientations correspond to a cusp in the boundary energy/misorientation plot, so does the  $\Sigma 13$  (32°) boundary. Nonetheless, the shrinking grains rotate through the  $\Sigma 13$  misorientation. During the rotation, calculation of the torque experienced by the grain boundary in conjunction with the instantaneous rotation rate enables us to extract the associated rotational mobility as well. Preliminary analysis suggests that the grain rotation mechanism is associated with diffusive effects and dislocation emission/absorption does not play any role during the rotation of these high-angle grain boundaries.

A new phase field model that includes an accurate description of grain boundary anisotropy was applied to simulate grain shrinking, as in the atomistic simulations. The atomistic results are used to determine parameters in the phase field model. The phase field simulations also show simultaneous grain boundary migration and grain rotation. Detailed comparisons between the atomistic and phase field results provide validation for the phase field approach as well as a method for determining its limitations.

## Semiconductor-Metal Heterophase Structures at High Pressures: Role of Interface Boundaries

Vladimir V. Shchennikov<sup>1</sup>, Sergey V. Ovsyannikov<sup>2</sup>

<sup>1</sup> *Institute of Metals Physics, Russian Academy of Sciences, Ural Division 620219  
Ekaterinburg, GSP-170, Russia*

<sup>2</sup> *Department of Physics, Ural State University, Ekaterinburg 620083, Russia*

In the vicinity of semiconductor-metal (S-M) phase transformations a sample may be viewed as a model of heterophase systems; most of their properties being dependent on the concentration and configuration of phases inclusions [1,2]. The approach to a real heterophases structures was developed by the ordered inclusions model with the variable phase configuration [1], and the calculations of the thermoelectric and galvanomagnetic properties were performed [2]. The relative dependencies of electrical resistivity on temperature and magnetic field  $\rho(T)$ ,  $\rho(B)$  above and below the threshold of SC-M transition, coincide with ones for  $M$  and  $SC$  phase excepting narrow interval of phase concentration  $c$  [3]. The threshold value of  $\rho$  for magnetoresistance  $MR$  is higher than that for  $M$ - $SC$  transition for any configuration of inclusions [2,3]. The results of calculations accord with experimental ones for metastable states of  $HgSeS$  and  $HgCdSe$  crystals, suffering  $M$ - $SC$  phase transitions at hydrostatic pressures  $P$  up to 2 GPa. The relatively high values of  $\rho$ , metallic-like dependence of  $\rho(T)$  and positive parabolic magnetoresistance  $MR$  effect of metastable state may be explained by the contributions of low pressure phase [2,3]. The existence of two phases at metastable states was proved by diffraction measurements at high pressures [4,5]. In the present paper the investigations of phase boundaries contribution was performed for heterophase systems under high pressures. The simple mixing of phases does not explain the change of the relative dependencies of electrical resistivity on magnetic field  $B$  and temperature  $\rho(B)$  and  $\rho(T)$  in contrary to the weakening of ones in experiment [3]. To fit experimental data by heterophase model one ought to assume that  $\rho(T)$  and  $\rho(B)$  dependencies of initial  $M$  phase is changing at mixing due to the increasing of the scattering centers concentration and the increasing of corresponding term  $\rho_0$  in  $\rho(T) = \rho_0 + \rho_1 T + \rho_2 T^2$ . The value of  $\rho_0$  corresponds probably to the interphases boundaries. The influence of interphase boundaries on thermoelectric power  $S$  and Hall-effect according to the model calculations and also high pressure experiments up to 30 GPa seems to be weaker compared with  $\rho(B)$  and  $\rho(T)$ . The using of the above approach made it possible to investigate the electronic and configuration parameters of phases in heterophase systems.

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## **Thermally Induced Changes of Interphase Boundary Morphology in Coherent A/B Multilayers: A Monte Carlo Simulation**

M. Bobeth, A. Ullrich, and W. Pompe

*Institut für Werkstoffwissenschaft, Technische Universität Dresden, Dresden, Germany*

Nanoscale A/B multilayers consisting of ferromagnetic layers separated by nonmagnetic spacer layers exhibit interesting properties as for example the giant magnetoresistance (GMR) effect. Large values of the GMR have been achieved for sputtered Co/Cu multilayers which show a columnar grain structure with grain sizes considerably larger than the individual layer thicknesses of 1 or 2 nm. The Co/Cu interphase boundaries within the grains are coherent. In order to improve the properties of as-deposited multilayers and to explore their thermal stability, experimental studies focused on the analysis of microstructure changes caused by annealing at elevated temperatures up to 700 °C. Since Co and Cu are largely immiscible, an intermixing does not occur. The aim of the present paper is to elucidate the conditions and mechanisms of a thermally induced destruction of multilayers by means of Monte Carlo simulations. The simulations are based on a vacancy migration algorithm and include the evolution of the phase morphology within the multilayer grains. Morphology changes are analysed in the vicinity of grain boundaries as well as in the grain interior far away from grain boundaries.

For polycrystalline A/B multilayers, layer decomposition is expected to start at grain boundaries by penetration of say component A into B layers which leads to break up of the B layers. Assuming that extended breakthroughs at grain boundaries are formed, we have simulated the subsequent evolution of the interphase boundaries in the adjacent multilayer grains. It was observed that during recession of a broken B layer a fusion with adjacent B layers takes place which, in turn, gives rise to recession of an A layer. In this way, characteristic sequences of recession, fusion and break up of layers develop. The resulting phase morphology depends on the characteristic time of initial layer break up at grain boundaries in comparison with the time for layer recession. In the case of antiferromagnetically coupled Co layers in Co/Cu multilayers, localised fusions of Co layers represent ferromagnetic short circuits and lead presumably to a strong deterioration of the overall GMR effect.

A high thermal stability of Co(2 nm)/Cu(2 nm) multilayers, sustaining 1 hour annealing at 400 °C, has recently been reported. Above 300 °C, the onset of a transition from a  $\langle 111 \rangle$  to a  $\langle 100 \rangle$  layer texture as well as of grain coarsening was detected. The observation of large lateral grain sizes after annealing at 400 °C, which exceed the individual layer thicknesses by two orders of magnitude, raises the question of the layer stability in the grain interior. Recent Monte Carlo simulations suggested that destruction of single crystalline multilayers starts by localised layer break up, which is presumably caused by thermal roughening of the interphase boundaries. The relevance of this intrinsic instability mechanism compared to layer break up at grain boundaries is discussed depending on individual layer thickness, temperature and layer orientation.

## **Influence of Near Surface Interaction $V_c$ -B During Low Temperature on Diffusion of B in SiC**

Ilkham G. Atabaev, Tojiddin M. Saliev, Erkin N. Bakhranov

*Physical Technical Institute of Uzbek Academy of Sciences,  
Mavlanov 2 B, 700084 Tashkent, Uzbekistan*

SiC is one of perspective semi-conductor materials for electrotechnics and optoelectronics. Now the large interest to SiC communicates with its luminescent properties. The number of articles are devoted to investigation of epitaxial n-SiC / Si structures. Usually, the epitaxial layers of SiC have n-type of conductivity (background impurity is nitrogen) with electron concentration  $10^{17-19} \text{ cm}^{-3}$ . The method to create p-n-junctions in SiC single-crystal usually used is the recrystallization from melted of a metal alloy or the diffusion Al or B at temperatures 1800-2300°C. It is obvious that if the n-SiC layer was grown on Si substrate the diffusion at high temperatures is impossible, as melting temperature of silicon is equal to 1417°C. The aim of this investigation is a search of the opportunity of diffusion of B in SiC at temperatures below 1400°C.

It is well known that the interaction of vacancies near surface can render essential influence to process of impurity diffusion in semiconductors.

In the presented article during diffusion of B in SiC the flow of vacancies  $V_c$  from a surface toward volume was created by special technology. Temperature of diffusion was 1100, 1150, 1200, 1250°C. The experiment was conducted on n-SiC / Si and n-SiC / SiC structures grown by CVD technology. Electron concentration in n-SiC layers  $10^{17-18} \text{ cm}^{-3}$ .

In the conditions of our experiment the anomalous high significance of the diffusion coefficient and solubility of B has observed ( $D \sim 10^{-10} \text{ cm}^2 / \text{sec}$  and  $N_B = 10^{17-18} \text{ cm}^{-3}$ ). As the diffusion process was perform in conditions of interaction of B atoms with  $V_c$  vacancies, the energy  $\epsilon_B$  of activation of diffusion of B at 1100-1250°C strongly differs from the  $\epsilon_B$  in the case of "ordinary" diffusion.

## **Grain Boundary Diffusion in Nanocrystalline and Nanostructured Metals: Models and Experiments**

M.B. Ivanov and Yu.R. Kolobov

*Institute of Strength Physics and Materials Science, SD RAS, Tomsk, Russia*

The experimental data on the investigations of grain boundary self- and impurity diffusion in pore-contained and pore-free nanocrystalline metals, as well as in the bulk nanostructured metals, processed by severe plastic deformation, were overviewed. The model of the diffusion along triple junctions as defects, which diffusion permeability may essentially exceed the respective of grain boundaries, was modified. The realization of the regime of type  $A_0$  during triple junction diffusion is predicted. The main feature of the above regime is the dependence of the effective measurable diffusivity on grain size of the material.

The influence of pores on the increase of diffusion permeability of grain boundaries and triple junctions in nanocrystalline materials is discussed.

## **Hydrogen Diffusion in Polycrystalline Silicon: Passivation and Depassivation of Grain Boundaries**

A. Fedotov<sup>1</sup>, E. Katz<sup>2</sup> and A. Mazanik<sup>1</sup>

<sup>1</sup>*Department of Energy Physics, Belarusian State University, Minsk, Belarus*

<sup>2</sup>*Department of Solar Energy and Environmental Physics,  
Jacob Blaustein Institute for Desert Research,  
Ben-Gurion University of the Negev, Sede Boqer Campus, 84990 Israel*

In contrast to single-crystals, polycrystalline silicon is an inhomogeneous material in which identical crystallites are separated by grain boundaries (GBs). Some of these two-dimensional interfaces accommodate high concentrations of strained Si-Si bonds and Si dangling bonds. During last decades a considerable effort has been dedicated to the passivation of GBs in order to improve electronic and optical properties of poly-Si. Hydrogenation, typically from a plasma sources, is usually used for this goal. However, published data concerning this topic are fragmentary and contradictory, showing a very complex mechanism for hydrogen diffusion in poly-Si. There are some processes which control the hydrogen penetration into a material: a GB diffusion, a diffusion into grains, a hydrogen capture by GB traps (mainly dangling bonds) and traps which are inside the grains, a hydrogen release from deep and shallow traps, the reaction  $2H \leftrightarrow H_2$ , a hydrogen interaction with GB electric and (or) elastic fields, generation of new defects under hydrogen exposure, etc. In other words, the consequences of hydrogenation will depend on relation between hydrogen diffusivities along GBs and in the grain bulk which is determined both by the state of poly-Si (a growing technique and heat treatments) and type of GBs (density and energy distribution of dangling bonds).

This paper presents the results of a detailed investigation which can shed a new light on the problems of relation between GB and grain-bulk diffusivities of hydrogen and passivation of grain boundaries of different type in poly-Si under exposure in hydrogen plasma.

The changes in GB electrical activity observed for both as-grown and annealed polycrystals were explained on the base of phenomenological model assuming that non-special GB act as channels with enhanced diffusion of hydrogen. Relation between diffusivities along GB and into grains, and as a consequence, relation between efficiencies of neutralization of GB deep traps and shallow acceptors (boron) in its grain neighborhood, are shown to be affected by the state of the crystal (as-grown or annealed). Passivation of boron is accompanied by the decreasing of screening a GB charge density and by increasing of the boundary barrier height (depassivation effect). This circumstance offers that in the annealed crystals whose hydrogen diffusivity is essentially lower than in as-grown ones the only a passivation of electrical activity of grain boundaries takes place. At the same time, in the as-grown crystals (where the grain-bulk diffusivity of hydrogen is much more higher than in annealed ones) processes of passivation and depassivation are in the progress simultaneously.

## **On The Theory of Diffusion in Grain Boundaries with Irregular Atomic Structure**

V.N. Perevezentsev

*Nizhny Novgorod Branch of Mechanical Engineering Research Institute RAS  
Ul. Belinskogo 85, Nizhny Novgorod, Russia 603024*

It is shown that diffusion characteristics of general grain boundaries (grain boundaries with disorientation far from special angles) are connected with a value of surplus boundary volume  $\Delta v_b$  which appear during absorption of vacancies by a boundary from a grain volume and their further delocalization in an irregular atomic structure of boundary. It is established that some surplus volume  $\Delta v_b^*$  exists and it is correspond to a minimum of free energy of boundary when boundary is in equilibrium with lattice vacancies. In the case of  $\Delta v_b < \Delta v_b^*$  – absorption of vacancies is energetically advantageous and in the case of  $\Delta v_b > \Delta v_b^*$  – emitting of vacancies from boundary to a grain volume. Grain boundary diffusion mechanism is considered as formation of metastable localized grain boundary vacancy due to a thermal fluctuation of material density in a volume contain  $m = \Omega_v / \Delta v_b$  atoms ( $\Omega_v$  – vacancy volume,  $\Delta v_b$  – surplus volume of boundary per one atom) and single jump of adjacent atom to vacancy. Expressions for coefficient of diffusion in equilibrium ( $\Delta v_b = \Delta v_b^*$ ) and unequilibrium ( $\Delta v_b > \Delta v_b^*$ ) grain boundaries are received. Possibility of considerable increasing of diffusion coefficient in unequilibrium grain boundaries is shown.

## **Wetting of Niobium and Iron Single Crystals by Low-Melting-Point Metals and Alloys**

Eugen Rabkin (1), Anatoliy Verhovlyuk (2), Oleksander Shcheretsky (2),  
Victor Witusevich (2), Valery Semenov (3)

*(1) Department of Materials Engineering, Technion, Haifa, Israel.*

*(2) Physico-technological Institute of Metals and Alloys of the NAS of Ukraine, Kyiv, Ukraine*

*(3) Institute of Solid States Physics of the RAS, Chernogolovka, Moscow district*

We studied the wettability of Nb and Fe single crystals by liquid metals and alloys that do not form the chemical compounds with them. High purity Pb, Cu, Ag, In, Pb-14.0 at.% Ag and Ag-28.0 at.%Cu were employed as starting materials after re-melting in vacuum.

Sessile drop wetting experiments were performed in high-purity helium atmosphere in the range of temperatures from the melting point of investigated alloys to 1200°C. The computer and CCD camera based system of automatic capture and processing of sessile drop image was used in experiments.

The temperature dependence of the surface energy and of the contact angle of liquid Ag, In, Pb, Ag-Pb and Ag-Cu on the single crystals of Nb and Fe were determined. The contact angles decrease with increasing temperature for all studied systems. Annealing of liquid Pb, In and Ag-Pb on Nb at the temperature of 1100°C during 10 minutes leads to the decrease of the wetting angle. Annealing of liquid Pb on the Fe single crystal at the temperature of 720°C for 35 min leads to the decrease of wetting angle from 100 down to 75 deg. Increasing the temperature up to 850°C causes further decrease of the wetting angles down to 60 deg.

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## **Free Electrons in Grain Boundary Wetting**

E. Rabkin and I. Snapiro

*Department of Materials Engineering, Technion, 32000 Haifa, Israel*

A quantitative description of the stability of nanometric thin liquid films at the grain boundaries in metals is given. The competition between the long-range van der Waals attraction and the short-range electrostatic repulsion of two solid-liquid interfaces results in an equilibrium liquid film thickness. The conditions for the existence of such an equilibrium thickness are considered. The electrostatic repulsion of two solid-liquid interfaces caused by the redistribution of free electrons between the grains and the intergranular film is treated in the framework of jelly model.

This simple model demonstrates an interesting behaviour, depending on the differences in electron densities and in Fermi energies of the solid and liquid phases.

The following experimental situations can be described:

- incomplete wetting of the grain boundary by the liquid phase;
- complete wetting of the grain boundary accompanied by the presence of nanometric equilibrium liquid film at the grain boundary;
- incomplete wetting accompanied by the presence of nanometric equilibrium liquid film at the grain boundary.

The experimental data for Ni-Bi and Cu-Bi systems are discussed in terms of suggested model.

## **Wetting of Grain Boundaries in Mo by the Ni-Rich Melt**

Boris B. Straumal, Valery N. Semenov, Sergei A. Polyakov

*Institute of Solid State Physics, Russian Academy of Sciences,  
Chernogolovka, Moscow District, 142432 Russia*

Liquid phase sintering is widely used for manufacturing of parts made from refractory alloys because the addition of metals with a lower melting temperature like Ni or Cu enhances drastically the consolidation process of Mo or W. In fact, the behaviour of liquid phase sintering depends critically on the competition between the diffusional and non-diffusional processes, like grain boundary (GB) migration, liquid film migration, and GB penetration of a liquid phase. The last process can proceed only if the dihedral contact angle in a triple point "GB – two solid/liquid interphase boundaries"  $\theta = 0$ . The temperature  $T_w$  can exist such that for  $T > T_w$  the contact angle  $\theta = 0$  and for  $T < T_w$   $\theta > 0$ . Above this temperature the GB is completely wetted by the liquid phase and penetration can occur, while at lower temperatures the wetting is incomplete and the liquid films along the GBs are not formed. This change at  $T_w$  has a name of GB wetting phase transition. The value of  $T_w$  is governed by the ratio of energies of GB and solid/liquid interphase boundaries. Above  $T_w$  GB cannot exist in the equilibrium with a liquid phase which must separate the individual solid grains. The behaviour of the liquid phase sintering has not been treated so far from the viewpoint of GB wetting phase transitions. This is due to the lack of information about the temperature dependence of the GB dihedral contact angle.  $T_w$  depends essentially on the GB energy. Therefore, the dependencies  $\theta(T)$  should be measured with the aid of individual GBs in bicrystals. Two [110] cylindric Mo bicrystals were grown in the vacuum floating zone melting apparatus from Mo of 99.95 wt.% purity. Tilt symmetric [110] GBs have the misorientation angles of 20° and 70°. The  $\langle 110 \rangle$  axes in both grains are parallel to the growth axis. The 2.5 mm thick platelets were cutted from the Mo bicrystals. The layer of Ni of 99.999 wt.% purity was applied in vacuum on the surface of the bicrystalline platelets and on the 0.5 mm thick polycrystalline 99.9 wt.% Mo foil with the aid of the splash electron beam heating. The bicrystalline platelets and the polycrystalline foil covered by nickel were then positioned on the sample holder made of  $\phi 1$  mm 99.9 wt.% Mo wire and annealed in the temperature interval from 1200 to 1780 °C. After quenching, the angles  $\theta$  at the contact of the GBs with the former solid-liquid interface were measured at the cross-section of the sample. The contact angles were measured for both Mo bicrystals, polycrystalline Mo foil and polycrystalline Mo wire. For each annealing temperature about 100 GBs were analysed in the polycrystalline foil and wire. The angle  $\theta$  for bicrystals and mean values of  $\theta$  for polycrystals decrease gradually from 180°C down to 0° with increasing temperature. It means that the GB wetting phase transition proceeds in the Mo–Ni system. Above 1360 °C all GBs are wetted by the melt. The grains in the Mo foil are completely separated from each other. First completely wetted GBs appear already at 1320 °C. The lines of the GB wetting phase transition were constructed in the bulk Mo–Ni phase diagram. The influence of the GB wetting phase transitions on the liquid phase sintering and semi-solid processing is discussed.

## **Diffusion Controlled Grain Boundary Wetting**

I. Apikhtina, B. Bokstein, A. Petelin

*Physical Chemistry Department, Steel and Alloys Institute,  
Leninsky Pr.4, 117936 Moscow, Russia*

The liquid grooving is very practical important process in all cases where there are the contacts between liquid and solid metals. In the theoretical plane this process is especially interest while it consists from some stages in solid and liquid phases. There are undoubtedly any diffusion stages – liquid diffusion, or surface diffusion, or crystal defect diffusion in solid metal. But there is no clearly thermodynamic and kinetic description of this process.

In this report is presented a short review, contained the theoretical and experimental data about grain boundary liquid grooving. It is proposed the thermodynamic consideration of the liquid grooves formation process. It is discussed the necessity of including in this consideration the Gibbs energy change by the mass transfer of the solid metal in the liquid phase. A few versions of kinetic models of grooving process are proposed. As one of the stages of the process is considered the grain boundary self diffusion in solid metal.

There are given own experimental results for systems: liquid bismuth – polycrystalline copper, liquid tin – polycrystalline aluminum. The corresponding points between experimental data and theoretical description are discussed.

## **Ion Beam Induced Smoothing – Mechanisms in Amorphous Materials**

Yinon Ashekanzy<sup>(1,2)</sup>, S.G. Mayr<sup>(2)</sup>, Y. Zhong<sup>(2)</sup>, R.S. Averbach<sup>(1,2)</sup>

<sup>(1)</sup>*Center for simulation of advance rockets,  
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

<sup>(2)</sup>*Dept. of Materials Science and Engineering,  
University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*

The control of surface roughness during the growth of thin film devices is of great importance in many technological applications. Roughness may develop through several competing mechanisms, such as surface diffusion, sputtering, and adatom addition, amongst others. We have been investigating the effects of ion beams on surfaces roughness using large scale molecular dynamics computer simulations and experimental methods. Our studies emphasize amorphous materials, as they are conducive to a full analysis of the problem, as well as being of vital importance in the development of semiconductor devices. Our investigations consider both low energy ( $E < 1$  keV) and high energy ( $E > 3$  keV) bombardment and include both covalent and metallic bonded systems. Two geometries are employed in the experiments and simulations: (i) spherical nanoparticles are placed on surfaces; (ii) sinusoidal surfaces of varying wavelength are created. In both cases, capillary forces drive the smoothing reaction by viscous flow, while sputtering and “microexplosions” cause roughening. This work follows the dynamics of these competing forces.

As an example we illustrate the smoothing reaction of a Cu nanoparticle deposited on an amorphous Cu-Ti substrate. This system can smooth by either the particle wetting the surface or by burrowing into the substrate as illustrated in Figs. 1 and 2. Here a crystalline Cu sphere, 2.4 nm in diameter, sitting on a  $\text{Cu}_{50}\text{Ti}_{50}$  substrate is subjected to repeated impacts with 40 keV Xe ions. As seen, the particle begins to wet the substrate but even more rapidly, it burrows. This is shown more clearly in Fig. 3 where the spatial distribution of atoms in the nanoparticle is presented. The surface energy of the nanoparticle and the viscosity of the substrate determine the rate of burrowing. From these MD simulations we can show that local heating by the irradiation causes a huge drop in the viscosity of the substrate which is nominally at 0 K. Experiments illustrating this behavior will also be presented.

In a second series of simulations and experiments, similar behaviors will be shown whereby a rough amorphous film is smoothed by ion irradiation. The amorphous surface lacks long-range structural order and lattice constraints, thus local diffusion barriers such as well-defined steps, which are dominant factors in many crystalline materials, are absent and allow one to study other mechanisms. In this case the processes are identified from scaling laws describing the surface height-height auto-correlation function as well as from direct simulation. Scaling laws stemming from simulation and experiments are compared.

## **Thermal Effects in Dynamics of Interfaces**

A. Umantsev

*Department of Materials Science, Northwestern University, Evanston, IL 60208.*

Moving interfaces are exposed to different thermal effects that were studied mainly for first-order transitions like melting-freezing and first-order structural transition where emission or absorption of the latent heat associated with the transformation renders a feedback reaction on the rate of transformation. Thermal effects may also alter the course of the structural evolution after a continuous transition or spinodal decomposition and change the rate of grain structure coarsening, especially in systems with low thermal conductivity. These effects stem from the existence of the surface internal energy and temperature gradients in the interfacial transition region.

The most convenient way to study different thermal effects of motion of interfaces is the paradigm of the Landau theory of phase transitions where one assumes that the Gibbs free energy is a continuous function of the long-range order parameter in addition to temperature, pressure and composition. In my presentation I will discuss how to apply the dynamical Ginzburg-Landau theory to the study of thermal effects of motion of interfaces that appear after different phase transitions. Evolution equations for the interfacial motion applicable in various situations will be derived on the common grounds. These equations identify the local interfacial variables like velocity, curvature, and jumps of temperature and temperature gradient across the interface, and relate them to the thermodynamic and kinetic properties of the medium like surface energy and thickness, latent heat, mobility and thermal diffusivity. For the experimental verification of the thermal effects the expression for the amplitude of temperature waves during continuous ordering will be presented.

## **Transition Zone Formation During Vacuum Deposition of Low Soluble Materials**

Faina Muktepavela<sup>1</sup>, Andris Simanovskis<sup>1</sup> and Sara Stolyarova<sup>2</sup>

<sup>1</sup>*Institute of Solid State Physics, University of Latvia, LV-1063, Riga, Latvia*

<sup>2</sup>*Solid State Institute, Technion, Haifa, Israel*

The aim of this work is to study the role of surface energy in the interface structure of metal/metal and metal/dielectric systems. Composition, electrical resistance, interface formation and aging kinetics of the binary Cu/Bi, Sn/Al, Pb/Ag and Ag/TlBr-TlI thin film systems have been investigated. Metal thin films have been obtained by thermal evaporation, for Ag/TlBr-TlI system plasma treatment of substrate surface has been applied prior to film deposition. The atomically-clean surfaces have been used in the present work for studying different interaction phenomena.

It has been found that the interface formed in the Cu/Bi, Sn/Al, Pb/Ag systems is drastically controlled by the surface energy of employed metals. If the top layer consists of the metal with lower surface energy, the interface is abrupt as expected for mutually non-soluble and compounds non-forming components. If the top layer consists of the metal with higher surface energy, a transition zone of 10 nm or more, is formed by intermixing of the two non-soluble materials. It is shown that the intermixing occurs during the island growth stage of the top layer by overlaying the growing islands with the base layer atoms via heterodiffusion mechanism.

The same effect can be also observed for metal deposition on compound substrate if some excess of metal component of the substrate is present at the substrate surface. This process was modeled by plasma treatment of TlBr-TlI crystal prior to Ag deposition. Due to selective plasma etching, a layer of Tl is formed on the TlBr-TlI surface. During the deposition of Ag film on this surface, a transition zone (~ 30 nm thick) is formed at the interface on the stage of Ag islands growth. The overlaying of Ag islands with Tl is observed, as in the case of mutually non-soluble metal films.

The process is thermodynamically gainful because the surface energy of Tl is lower than that of Ag and the Ag/Tl interface energy has relatively small value.

## **Microstructural Dependence of Giant-Magnetoresistance of Electrodeposited Cu-Co Alloys**

Tzipi Cohen-Hyams<sup>1</sup>, J. M. Plitzko<sup>2</sup>, Wayne D. Kaplan<sup>1</sup> and Joseph Yahalom<sup>1</sup>

<sup>1</sup>*Department of Materials Engineering, Technion, Haifa, Israel*

<sup>2</sup>*Lawrence Livermore National Laboratory -University of California, Berkeley*

One of the most exciting and startling properties exhibited by some magnetic multilayer systems is the giant-magnetoresistance (GMR) effect. GMR refers to a significant change in the electrical resistance of a film or a device when an external magnetic field is applied [1]. GMR has been observed in many *multilayered* structures [2] and also in heterogeneous alloys with ferromagnetic granules (for example: Fe, Co) embedded in a non-magnetic metal (for example: Cu or Ag). The heterogeneous alloy films are immiscible combinations usually prepared by physical and electrochemical methods [3-5], which are subsequently heat treated causing the precipitation of small ferromagnetic particles in a medium of a non-magnetic matrix.

The aim of the present research is to investigate the fundamental interrelationship of the microstructure with the magnetic properties of electrodeposited Cu-Co system. Preliminary results from X-ray diffraction (XRD) showed that the electrodeposition process is a topotaxial crystallization process and that the as-deposited film is composed of two phases, a solid solution of fcc Cu-Co with preferred orientation of {111} planes, and a hcp Co phase. Scanning electron microscopy (SEM) micrographs combined with energy dispersive spectroscopy (EDS), electron energy loss spectroscopy (EELS), and elemental mapping via electron spectroscopic imaging (ESI) revealed the development of the cobalt microstructure as a function of thermal treatments. Cobalt diffuses away from the solid solution of Cu-Co alloy forming cobalt precipitates, according to the phase diagram of Cu-Co. Furthermore, a continuous thin layer of cobalt is formed with increasing annealing time.

The largest value of the GMR effect was observed after annealing at 450°C for 90 min. The magnetic properties closely correlate with the microstructure, mainly with cobalt magnetic particle size and its distribution.

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## **On the Correlation of Grain Boundary Segregation in Intermetallics**

Pavel Lejcek<sup>1</sup>, and Anna Fraczkiewicz<sup>2</sup>

<sup>1</sup>*Institute of Physics, AS CR, Praha, Czech Republic*

<sup>2</sup>*Ecole Nationale Supérieure des Mines, St. Etienne, France*

It is generally accepted that presence of boron in ordered intermetallic alloys such as Ni<sub>3</sub>Al, NiAl and FeAl, enhances their ductility. It is proved that in these materials, boron segregates at grain boundaries and forms directed bonds with the matrix atoms parallel to the boundary plane [1,2]. The experimental studies of grain boundary segregation in intermetallics suggest, however, that grain boundary saturation occurs despite of the bulk content of boron. Recently, a concentration dependence of equilibrium boron segregation at grain boundaries of polycrystalline Fe-40at.%Al base intermetallics was measured at 400°C [3]. In this study, the saturation of grain boundaries at the level of about 13 at.% of boron was also reported corresponding to the bulk content of this segregant of 800–2000 at.ppm that is beyond the limit of its solid solubility in this material.

In the present contribution, two methods of correlation of experimental data on grain boundary segregation of boron in intermetallics are compared: the Fowler segregation isotherm and the Langmuir–McLean isotherm considering reduced number of grain boundary positions available for segregation [4]. It is shown that the latter approach provides physically acceptable results and the limited number of segregation positions can be explained by a high degree of the order of the system. A comparable correlation according to the Fowler isotherm requires large positive interaction parameter suggesting strong repulsion of boron atoms which seems to be physically improbable. The capability of both types of correlation is documented on recent experimental data on boron segregation at grain boundaries in FeAl and Ni<sub>3</sub>Al base intermetallics.

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## **Auger Electron Spectroscopy Investigation of Sulfur Surface Segregation on Nb (110) and Nb (111)**

Bakhtiyar Atabaev<sup>1</sup>, Nilufar Saidkhanova<sup>1</sup>, Sherali Khojiev<sup>1</sup>, Eugen Rabkin<sup>2</sup>,  
and Valery Semenov<sup>3</sup>

<sup>1</sup>*Arifov Institute of Electronics, Tashkent, Uzbekistan.*

<sup>2</sup>*Department of Materials Engineering, Technion, Haifa, Israel.*

<sup>3</sup>*Institute of Solid State Physics, Chernogolovka, Russia.*

The segregation of impurities to the free surfaces of metals is a subject of intensive studies, however, relatively little is known about the dependence of parameters of surface segregation on the surface orientation. The most important parameter characterizing the surface segregation of impurities is the enthalpy of segregation, which is the measure of the difference in the internal energy of the segregated species at the surface and in the bulk of a 3D phase. The segregation enthalpy could be determined from an Arrhenius plot of the temperature dependence of the experimental values of impurity concentration ratios at the surface and in the bulk. We present here the experimental studies of surface segregation of sulfur on niobium (110) and (111) surfaces. The measurements were performed in a stainless-steel UHV system at a base pressure of  $7 \times 10^{-8}$  Pa. After argon ion sputtering, the oxygen and carbon signals were greatly reduced, but still present because of the presence of residual gases.

The heating of the sample from room temperature up to 1400 K led to the segregation of sulfur at the surface, so that the sulfur Auger peak became higher than that of niobium. The sulfur segregation in the as-received samples was not observed until 700 K and then dramatically increased. Simultaneously, the disappearance of the oxygen and carbon was observed. This suggests that the oxygen and perhaps the carbon forced sulfur to stay in the bulk until dissolution of the oxygen and carbon occurred.

The segregation of sulfur at Nb(110) and Nb(111) surface was investigated by measuring the temperature dependence of the relative Auger peak heights. The atomic concentration of the sulfur was calculated from the AES spectrum by using elemental sensitivity factors from the literature. Auger electrons were recorded with a cylindrical mirror analyzer IOS.

The measured value of surface coverage (SC) of sulfur on niobium at maximum segregation are SC=0.36 and SC=0.9 for S/Nb(111) and S/Nb(110), respectively. This suggests that sulfur segregation is strongly orientation-dependent. For the temperatures above 700 K the dependence of the logarithm of the ratio of S Auger peak at 152 eV to the Nb peak at 167 eV on reciprocal temperature is linear. The corresponding activation energies are  $E_s = 0.66 \pm 0.1$  eV for S/Nb(110) and  $E_s = 0.39 \pm 0.1$  eV S/Nb(111).

The obtained sulfur segregation temperature 700 K agrees well with temperatures observed previously for the other metals. The measured values of  $E_s$  are higher than those found for sulfur surface segregation on the other metals, e.g. on nickel or on tungsten. Our results suggest that there is a strong competition for the surface segregation sites in Nb between the sulfur from the one side, and oxygen and carbon from the other side.

The high segregation level on the closely packed (110) plane implies that the number of surface segregation sites is the most important factor determining the amount of S segregation on the surface of Nb.

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## **Segregation of Aluminum at Nickel-Sapphire Interfaces**

G. Levi<sup>1</sup>, W. D. Kaplan<sup>1</sup> and C. Scheu<sup>2</sup>

<sup>1</sup> *Technion, Israel Institute of Technology, 32000 Haifa, Israel*

<sup>2</sup> *Max-Planck-Institut für Metallforschung, D-70174 Stuttgart, Germany*

There has been a long tradition of trying to extract thermodynamic data from contact angles of liquid metals on ceramic substrates. However, to understand the mechanisms governing interface adhesion at a metal-ceramic interface, it is necessary to conduct model experiments under controlled conditions, *combined* with detailed investigation of the structure and chemistry of the interface.

Sessile drop experiments of liquid pure Ni and Ni slightly alloyed with Al on the (0001) plane of sapphire (pure single crystal  $\alpha$ -alumina) were conducted under a controlled atmosphere and temperature. Images of the liquid drops on the sapphire substrates were recorded in-situ, as a function of temperature. After cooling, the morphology, structure and chemistry of the samples from the experiments were studied using imaging and analytical electron microscopy, with emphasise on the interfacial region. Very high spatial resolution chemical analysis was conducted at the interface region, in cross-section, on a VG HB501 dedicated scanning transmission electron microscope using energy dispersive spectroscopy and parallel electron energy low loss spectroscopy.

The high spatial resolution chemical analysis shows the presence of a relative large quantity of Al in Ni, at the Ni-sapphire interface, and use of the spatial difference technique indicates the existence of an *excess* of Al *segregated* at this interface. Based on the microstructural evidence it is concluded that the sapphire substrate undergoes capillary driven dissolution during wetting, resulting in the release of Al into the liquid Ni. Al freed into the liquid Ni segregates to the free surface of the liquid Ni, and to the Ni-sapphire interface where it apparently forms more than one monolayer of pure Al. Alloying of liquid Ni with Al significantly reduces the Ni-sapphire interface energy, and enhances the interface strength after solidification. It is considered that lowering of the interface energy and increase in the interface strength in Ni(Al)-sapphire system is due to the *segregation* of Al.

## **Grain Growth During Superplastic Deformation**

Michael Zelin<sup>1</sup>, Boris Gershon<sup>2</sup> and Itzhak Arbel<sup>2</sup>

<sup>1</sup>*Adan, Inc., Canal Fulton, OH 44614, USA.*

<sup>2</sup>*Israel Aircraft Industries, LTD, ISRAEL.*

Rate of strain induced grain growth during superplastic deformation significantly exceeds that of static grain growth. Such a high grain growth rate under superplastic conditions is typically attributed to a high mobility of grain boundaries. For example, over saturation of grain boundaries with vacancies or non-equilibrium state of grain boundaries have been shown to increase grain boundary diffusivity resulting in a higher grain boundary mobility.

Data and analysis presented in this paper indicate that high grain growth rate under superplastic condition can also result from a high driving force related to the micro-mechanism of superplastic flow. Specifically, cooperative manner of grain boundary sliding, i.e. sliding of grain groups, occurring during superplastic deformation is accompanied by cooperative grain boundary migration. Sliding grain boundary segments forming macroscopic shear bands also migrate in a cooperative manner. Such a long range correlation in migration of grain boundaries is caused by coupling of grain boundary sliding and migration. At the scale of grain boundaries, this can be modeled in terms of movement of grain boundary dislocations that have a step associated with its core.

Results obtained in a Pb-62%Sn alloy, AA7475 aluminum alloy, and a Ti-alloy support cooperative manner of grain boundary migration during superplastic deformation. Observations performed on the deformed surface of superplastically deformed tensile and shear Pb-62%Sn samples and bi-axially formed AA7475 samples directly showed coupling between grain boundary sliding and migration. Observed correlation between grain size and strain measured in different regions of a superplastically formed Ti-alloy part also supports coupling of grain boundary sliding and migration as a major mechanism for grain growth during superplastic deformation.

## **Influence of Microstructure and Grain Boundaries on the Mechanical Properties and Failure of Steel St3**

M.N. Nazarova<sup>1</sup>, E.A. Vdovin<sup>2</sup>, N.K. Tsenev<sup>2</sup>, B.E. Selskii<sup>2</sup>

<sup>1</sup>*Institute for Metals Superplasticity Problems, Russian Academy of Sciences,  
39, Khalturina str., 450001 Ufa, Russia.*

<sup>2</sup>*Ufa State Petroleum Technical University,  
1, Kosmonavtov str., 450062 Ufa, Russia.*

This work investigates structure evolution in low-carbon ferrite-pearlitic steel ST3 (Russian grade) (Fe-0.17%C-0.5%Mn-0.2%Si-0.03%P-0.04%S) during high temperature annealing and alternate deformation, its influence on mechanical properties and development of failure processes.

Metallographic methods showed that annealing of the steel at temperature (1070 K) results in refinement of ferrite grains and pearlite. Further annealing at 1320 K lead to dissolution of pearlite. The performed mechanical tests indicated that refinement of pearlite and ferrite leads to enhancement of mechanical properties and dissolution of pearlite results in their decrease.

Alternate deformation by flexure allowed to fabricate a cellular structure and a structure with “knife” type grain boundaries which are characterised by smoothly bent, very thin and perfect grain boundaries. This boundaries form high angle misorientations of neighbouring interface which attain several dozens degrees.

It has been shown that of microfragment boundaries structure in ferrite grains influence noticeably on the character of steel failure. In case of the appearance of “knife” type boundaries the percentage of ductile fracture decreases in 30-40% during impact tests. The effort employed during failure tests considerably decreases.

The present work discusses the influence of grain boundary structure on mechanical properties and the failure character in low-carbon steel.

## Faceting and Roughening of the Asymmetric Twin Boundaries in Zinc

Boris B. Straumal, Vera G. Sursaeva, Sergei A. Polyakov

*Institute of Solid State Physics, Russian Academy of Sciences,  
Chernogolovka, Moscow District, 142432 Russia*

Faceting is a well documented phenomenon known both for surfaces and interfaces, particularly, grain boundaries (GBs). Faceting can be considered as a phase transition when the original surface or GB dissociates onto flat segments whose energy is less than that of the original surface or GB. GB faceting can be observed only close to the so-called coincidence misorientations. In this case the lattices of both grains form the coincidence site lattice (CSL) characterized by the parameter  $\Sigma$  (reverse density of coincidence sites). In most cases the GB facets lie in the CSL planes with high density of coincidence sites. Zn  $[11\bar{2}0]$  flat single crystals were grown using the modified Bridgman technique from Zn of 99.999 wt.% purity. Individual elongated twin plates having very uniform thickness were produced with the aid of slight deformation of single crystals. The produced twin plates are perpendicular to the surface of the sample and possess a very uniform thickness. The  $[11\bar{2}0]$  axes in both grains are also perpendicular to the surface of the sample. The parallel long sides of the twin plate are formed by the symmetric twin GBs or  $(100)_{\text{CSL}}$  facets. Due to its optical anisotropy, zinc allows one to study the shape of the GB with the aid of polarized light. The stationary shape of the slowly migrating tip of the twin plate has been studied *in situ* in the hot stage of optical microscope in the temperature interval from 317 to 417 °C. It has been shown that below 357 °C the twin tip contains only one plane facet, namely asymmetric twin GB  $(010)_{\text{CSL}}$ . The  $(010)_{\text{CSL}}$  facet has the angle of about 86° with the symmetric twin  $(100)_{\text{CSL}}$ . Above 357 °C the second facet  $(110)_{\text{CSL}}$  appear at the tip of the twin plate. The second  $(110)_{\text{CSL}}$  facet in the twin tip has the angle of about 45° with the symmetric twin  $(100)_{\text{CSL}}$ . By temperature increase from 357 to 412 °C the length ratio of  $(010)_{\text{CSL}}$  and  $(110)_{\text{CSL}}$  facets increases from 0 to 1. Above 412 °C only one  $(110)_{\text{CSL}}$  facet is present in the twin tip. The indications of the GB roughening phase transition were also observed, namely the corners of the facets become smoother with increasing temperature. The GB phase diagram for the twin GBs in zinc containing the lines of GB faceting and GB roughening phase transition has been constructed. In [1] it has been shown that the GB possess the special structure and properties in the limited areas of temperature  $T$  and misorientation  $\theta$  close to a coincidence misorientation  $\theta_{\Sigma}$ . In other words, by increase of  $\Delta\theta = |\theta - \theta_{\Sigma}|$  and  $T$  the phase transition „special GB – general GB“ proceeds and GB loses its special structure and properties. The ratio of  $a$  and  $c$  spacings in Zn is not rational and is temperature dependent. Therefore, the GB  $(010)_{\text{CSL}} - (010)_{\text{CSL}} + (110)_{\text{CSL}} - (110)_{\text{CSL}}$  GB faceting transition can be driven by the  $c/a$  temperature dependence of the constrained CSL structure.

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## **Interphase Boundaries and Anisotropy via Multiple-Order-Parameter Theory for an FCC Alloy**

G. Tanoglu\* R.J. Braun\*\*,

*\* Izmir Institute of Technology, Department of Mathematics  
Gülbağçe kampüs, 35437, Urla, Izmir, Turkey*

*\*\*University of Delaware, USA*

The anisotropy of interphase boundaries (IPBs) and antiphase boundaries (APBs) in a binary alloy on an fcc lattice was studied using a recently developed diffuse interface model that uses three nonconserved order parameters and one conserved order parameter, the concentration. This model has the capability of modeling one disordered and the two ordered phases ( $L1_2$  and  $L1_0$ ) that occur in the Cu-Au system, the phase diagram, and the IPBs and APBs for all orientations with respect to the underlying lattice.

The behavior of the IPBs in the neighborhood of the  $L1_2$  and  $L1_0$  congruent points as well as the possibility of wetting near the eutectoid is illustrated with numerical results. Realistic interfacial energy anisotropy for the IPBs is obtained. The equilibrium shapes of  $L1_2$  and  $L1_0$  particles in the fcc matrix are also computed when elastic mismatch energy can be ignored.

## **Compensation Effect for Grain Boundary Diffusion in Bicrystalline Experiments**

A.N.Aleshin<sup>(1,2)</sup>, R.G.Faulkner<sup>(2)</sup>, D.A.Molodov<sup>(3)</sup>, and L.S.Shvindlerman<sup>(1,3)</sup>

- (1) *Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region 142432, Russia*
- (2) *Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK*
- (3) *Institut für Metallkunde und Metallphysik, RWTH Aachen, D-52056 Aachen, Germany*

X-ray microanalysis is used to study the grain boundary (GB) diffusion of Zn in Al bicrystals with  $\langle 100 \rangle$  and  $\langle 111 \rangle$  tilt boundaries with predetermined crystallographic parameters. It is shown that GBs in the vicinity of and far beyond  $\Sigma 7$  and  $\Sigma 13$  special misorientation provide a significant variation of the value of the triple product  $K\delta D_b$  ( $K$  is the GB enrichment ratio,  $\delta$  is the grain boundary width and  $D_b$  is the GB diffusion coefficient). The triple product is obtained from the measurements using Le Claire approach. The variation of the value of GB width,  $\delta$ , and the value of the enrichment ratio,  $K$ , due to GB structure change are estimated. It is concluded that  $D_b$  is the main GB structure sensitive parameter in the triple product. This circumstance allows us to consider the GBs in Al bicrystals as a set of the uniform objects and treat the kinetics of the GB diffusion in terms of so called compensation effect (CE), namely in the terms of the compensation temperature,  $T_c$ , and the "barrier" phase. The paper presents the experimental data on the GB diffusion of Zn [1] and Ge [2] in Al bicrystals with  $\langle 100 \rangle$  and  $\langle 111 \rangle$  tilt boundaries as a linear dependence of the preexponential factor on the activation energy for the GB diffusion. It is established that the value of the compensation temperature,  $T_c$ , for the GB diffusion of Zn and Ge in Al bicrystals is practically the same and equals 434 and 433 °C respectively. The character of "barrier" phase is discussed.

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2. T.Surholt, D.A.Molodov and Chr.Herzig, *Acta Materialia*, V.46, No15, pp. 5345 – 5355 (1998).

## **Grain Boundary Diffusivity and Creep of Nanostructured Metals and alloys**

Kolobov Yu.R.

*Institute of Strength Physics and Materials Science, SD RAS, Tomsk, Russia*

The main features of grain boundary diffusion of substitution impurities from external source (coating) in nanostructured (processed by severe plastic deformation) metals (nickel, copper, titanium) in comparison with coarse-grained and nanocrystalline (electrodeposited nickel) ones are considered. The physical reasons of the essential (by some orders of magnitude) increase of grain boundary diffusion permeability in nanostructured state relative to coarse-grained metals and bicrystals are disputed. The effect of creep activation by grain boundary diffusion fluxes of impurities in nanostructured metals in comparison with those in coarse-grained polycrystalline metals is discussed. The analysis of the role of grain boundary diffusion fluxes in realisation of structural superplasticity of polycrystalline and nanostructured metals and alloys is carried out.

## Grain Boundary Grooves as the Carriers of Electromigration

M. Nathan<sup>1</sup>, M. Khenner<sup>2</sup>, A. Averbuch<sup>2</sup>, and E. Glickman<sup>1</sup>

<sup>1</sup>*Department of EE-Physical Electronics, Tel Aviv University, Israel*

<sup>2</sup>*Department of Computer Science, Tel Aviv University, Israel*

Interface electromigration (EM) in thin metal film conductors is one of the most severe reliability concerns in ULSI microelectronics. One of the open questions in the theory of EM is how EM diffusional flux  $I_{GB}$  along grain boundaries (GBs) should be coupled to the surface diffusional flux  $I_s$  to account for a *uniform* EM displacement of the cathode edge, the process that is responsible for EM contact failures.

We suggest GB grooving to be such a coupling mechanism. The surface curvature gradients  $\nabla K$  and the electric field  $E$  along groove walls are the driving forces for two components of the flux  $I_{SK} + I_{SE} = I_s$  directed towards the groove tip. It is assumed that (i) permanent equilibrium between the surface tension and GB tension exists at the tip, and (ii) the flux  $I_s$  is coupled at the tip to  $I_{GB}$ .

The second assumption means that the groove tip serves as a *trans-shipping point* because all material delivered from the free surface to the tip by  $I_s$  goes then into GBs. As a result, the receding surface can displace uniformly being only slightly scalloped with small grooves, while the groove tip separation from the free surface remains constant with time.

We present a numerical simulation of the problem based on the Level Set method and applied the results to the analysis of recent drift velocity (DV) EM data for polygranular Cu interconnects. The numerical algorithm is formulated along the lines of previously proposed approximate analytical models by incorporating the flux  $I_{SE}$ .

Using independent, literature diffusivity values, and the simulation yields both the DV prefactor and DV activation energy. An excellent match is obtained with the experimental DV values in the T range 573-723K.

Remarkably, this agreement is achieved with ignorance of the role of surface and film/substrate interfaces as alternative EM pathways acting *in parallel* with GBs. Instead, the simulation emphasizes the role of surface diffusion along *freshly created* groove walls. This coupling process enables GB grooves to act as the EM carriers, via redistribution of the “emptiness” caused by the flux  $I_{GB}$  at each GB, over the free surface.

## **Mobility of Interfaces in Reactions of Thin Films of Metallic Glasses with Silicon Substrates**

Nikolay V. Rozhanskii, Vladimir O. Livshits

*Institute of Physical Chemistry, Russian Academy of Sciences  
Leninsky pr. 31, 119991 Moscow, Russian Federation*

Thin films of metallic glasses can be used as diffusion barriers in metallization circuits on Si since the diffusion of components in amorphous films is much slower than in polycrystalline ones. However diffusion processes in the amorphous state are studied not in detail as comparing with crystalline materials.

This work is connected with TEM studies of solid state reactions of sputter deposited Pd-W, Pd-Ta and Ni-Nb films with Si(100), (111) substrates. In-situ and ex-situ experiments on cross-sections and plan-view samples were performed in Philips 400T microscope equipped with a LINK-860 EDX spectrometer and a SEM/STEM system. Mobility of interfaces in Pd-Ta/Si(100) reactions were studied on corresponding cross-sections. Some concentration profiles of diffusing components were obtained by AES method with a use of an ESCALAB 5 apparatus.

We observed that films of Pd-Ta, Pd-W, and Ni-Nb alloys interacted with a Si substrate in the amorphous state with a formation of epitaxial silicide islands. The part of islands on the Si(100) substrate (or all of them in the case of a Si(111) orientation) start to dissolve with time and temperature. This feature is accompanied by the Si and Pd(Ni) diffusion back into the film on the contrary of a previous diffusion of metallic atoms inside the substrate.

High temperature reactions of Pd-Ta films with Si crystals are followed by the change of films structures: films start to crystallize at the inner interface with a growth of the crystalline layer with time and temperature. This layer presents a mixture of narrowest layers of Ta or Pd silicides. At the same time we observed the change in the structure of the rest of the film: an amorphous zone. The amorphous film decomposes into two different amorphous zones with various contrast and halos on diffraction patterns. TEM studies of the mobility of crystalline/amorphous interfaces on Pd-Ta/Si cross-sections permitted us to estimate diffusion parameters (activation and relaxation energies, diffusion coefficients) of Pd in amorphous Pd-Ta alloys. Mobility of interfaces in the amorphous zone seems to be connected with Si diffusion into the film.

As a result we showed that TEM was a powerful and very informative method in the study of interface reactions and phase transformations of amorphous metallic films with Si substrates.

## Compensation Effect for Kinetic Properties of Triple Junctions

V. G. Sursaeva, S. G. Protasova

*Institute of Solid State Physics, Russian Academy of Sciences,  
142432 Chernogolovka, Russia*

The compensation effect or Meyer-Neldel rule (MNR) is observed in wide range of phenomena. MNR appears to be a fundamental property of many families of activated processes following an Arrhenius dependence on temperature. The kinetic properties of grain boundaries (GBs) and triple junctions (TJs) in solids strongly depend on their crystallographic parameters and obey the Arrhenius law. Therefore, the GBs and TJs form the families of objects where the Meyer-Neldel behaviour of thermally activated processes can be easily observed.

The individual tricrystals were grown using the modification of Bridgeman technique. For the investigation TJ mobility, the special geometry of tricrystal is used. The velocity of moving TJ was measured *in situ* using the x-rays diffraction or polarized light. In all cases studied the TJs possess the higher  $H$  values than those of comparable individual GBs. The pretty well MN-behaviour was observed in all cases. In case of  $\langle 110 \rangle$  tilt TJs in Al the  $T_C = 490^\circ\text{C}$  ( $T_C/T_{\text{melting}} = 0.82$ ) and lies inside the studied temperature interval  $470\text{--}590^\circ\text{C}$ . In case of  $\langle 100 \rangle$  tilt TJs in Al the  $T_C = 520^\circ\text{C}$  ( $T_C/T_{\text{melting}} = 0.85$ ) lies inside the interval  $460\text{--}610^\circ\text{C}$ . In case of  $\langle 111 \rangle$  tilt TJs in Al the  $T_C = 460^\circ\text{C}$  ( $T_C/T_{\text{melting}} = 0.79$ ) lies inside the interval  $400\text{--}510^\circ\text{C}$ . This fact leads to the complicated behaviour of the mobility of tilt TJs with different misorientation of elongated tilt GBs. Namely, the maximum of mobility appears for TJs with high angle elongated tilt GB at temperatures  $T < T_C$ . This maximum of  $A$  disappears at  $T > T_C$ . The same behaviour was observed for  $\langle 111 \rangle$  tilt GBs close to the  $\Sigma 7$  coincidence misorientation  $38.2^\circ \langle 111 \rangle$ . Namely, the maximum of mobility appears at  $38.2^\circ$  at low temperatures. This maximum of  $A$  disappears at  $T > T_C$ . Therefore, the MN-behaviour of  $\langle 111 \rangle$  tilt GBs and TJs in Al can be attributed to the GB phase transitions rather than to the bulk ones. This hypothesis is supported also by the behaviour of  $\langle 11\bar{2}0 \rangle$  tilt GBs in Zn. The values of activation enthalpy of Zn twins are definitely higher than those of the  $\langle 11\bar{2}0 \rangle$  tilt GBs. However, both groups of GBs possess the same  $T_C = 350^\circ\text{C}$  ( $T_C/T_{\text{melting}} = 0.9$ ). This temperature lies, like in case of tilt TJs in Al, below the melting point and inside of the temperature interval studied  $200\text{--}419^\circ\text{C}$ . Both in case of Al TJs and TJs in Zn the compensation temperature differs from that of respective GBs. Such behaviour can be explained by the possible GB phase transitions among the various constrained-CSL GB structures. The intriguing high  $H$  values in Zn force the investigator to think about possible mechanisms of TJs migration. Both in case of  $\langle 100 \rangle$  and  $\langle 110 \rangle$  Al TJs and TJs in Zn the compensation temperature differs from that of respective GBs. This fact and the high  $H$  values for TJs support the suggestion that the TJs migration is controlled by the processes in TJ itself and not by the mobility of GBs forming the TJ.

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## **Interaction of Solute Impurity with Grain Boundary - Solute Drag**

Arkady Vilenkin

*The Racah Institute of Physics, The Hebrew University of Jerusalem, Israel.*

We consider an easy case of slow migrating grain boundary in poly-crystal contains solute impurity. Lucke, Stuve, and J. Cahn have done the well-known analysis of this problem. It is based on assumptions that 1) the grain boundary is a well for impurity atoms, 2) the width of the well is much larger than a lattice parameter, and it allows use of continuous mathematics. The second assumption seems to be very rough approximation, and it is important, because only atoms placed in the well generate drag force in the models. These papers do not contain any discussion about accuracy of the results based on these assumptions, and it is not clear which part of the results is excess of accuracy.

Brener and Temkin considered this problem on the basis of conventional physics, but they did not derive a kinetic equation, which is why there is no distinction between kinetic coefficients and thermodynamic driving force in the result.

We tried here to apply methods of conventional physics to obtain a kinetic equation in the case when unity of length is much larger than lattice parameter. A grain boundary is represented in this case by infinitely thin interface, which is characterized by two thermodynamical quantities: grain boundary energy and segregation coefficient. Use of such phenomenological description allows deriving an equation of grain boundary motion in binary poly-crystal. The derivation is based on Ginzburg-Landau conjecture about rate of minimization of total systems' free energy. The equation coincides in particular case of one component poly-crystal with well-known Mullins' equation of grain boundary migration driven by mean curvature. Another particular form of the equation has been used for an analysis of DIGM phenomenon.

An application of the equation to impurity drag effect problem requires introduction of two kinetic coefficients characterize a rate of solute impurity exchange between grain boundary and adjacent grain. We represent a traveling wave solution of formulated problem for a grain boundary driven by constant external force. The accuracy of the problem and its solution is  $O(v^2)$ , i.e. it is correct for small driving force.

It is shown, that sign of impurity effect on grain boundary velocity (delay, or acceleration) does not depend on kinetic coefficients. The sign of the effect is determined by the values of the grain boundary segregation coefficient, the derivative of grain boundary energy with respect to absorbed impurity concentration, and the derivative of bulk free energy with respect to bulk impurity concentration in grains.

## **Kinetics of Corrugated Anisotropic Surfaces**

L. Klinger and E. Rabkin

*Department of Materials Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel*

We study the flattening of corrugated crystal surface for the case when mass transport is driven by surface diffusion and the surface itself is strongly anisotropic. We adopt an approach in which the orientation of initial, non-perturbed surface corresponds to the deep singular cusp on the otherwise spherical surface energy  $\gamma$ -plot. We formulated a system of non-singular differential equations describing the temporal evolution of corrugated surface. The approximate analytical solution of these equations for the case of slow diffusivity along the singular surface is found with the help of perturbation theory. It demonstrates that the time for complete smoothing of the corrugation is finite, in sharp contrast with the previous treatments of the problem. For the long annealing times, the amplitude of corrugation decreases with time,  $t$ , according to the  $a-bt^{0.25}$  law, where  $a$  and  $b$  are constants. We discuss also the process of the nucleation of a facet at the initial stages of the annealing.

## Triple Junctions Effect on the Grain Growth in Nanostructured Materials

Protasova S., Sursaeva V.

*Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district, 142432, Russia*

The presented paper concerns the influence of triple junctions on the normal grain growth in nanostructured aluminium films. Microstructure evolution and grain growth in nanostructured aluminium films has been examined. The films were produced by vacuum evaporation on NaCl (100) substrate. It has been revealed that in the films the normal grain growth takes place. The obtained data on the normal grain growth were compared with those for 2-D aluminium strips and foils. Properties of polycrystalline materials are strongly influenced by their structure, namely by mean grain area, grain size distribution and the distribution of grain orientation. In turn these latter are determined by grain nucleation and grain growth. Grain growth proceeds by generation and migration of grain boundaries and triple junctions. Grain boundaries and triple junctions are not alike in their properties, especially in their kinetics. To manage the microstructure during grain growth it is necessary to understand what determines the kinetics of motion: grain boundaries or triple junctions. It is important in nanostructured materials, where grain boundaries and triple junctions make up a considerable part of the structure. In all studies concerning grain boundary migration and grain growth it was assumed that triple junctions do not have any influence on the motion of the boundaries, and their role in this process was reduced to establish the thermodynamic equilibrium angles at the junction during boundary motion.

Recently we have carried out investigations of individual triple junction motion in Al tricrystals and shown the motion kinetics of the system of grain boundaries with a triple junction depends on its temperature. There is  $T_{\text{transition}}$  - temperature of transition from grain boundary kinetics to triple junction kinetics. For the most of the individual triple junctions in aluminium  $T_{\text{transition}} > 500^\circ\text{C}$ . The effect of triple junction on grain boundary motion is determined by the dimensionless criterion  $\Lambda$ :

$$\Lambda = \frac{m_{TJ}a}{m_{GB}},$$

where  $m_{TJ}$  and  $m_{GB}$  are the mobilities of triple junction and grain boundaries correspondingly,  $a$  – grain size. The value of mean grain boundary mobility at a given temperature is distinctly lower for fine grained (films) than for coarse grained (strips) microstructures, and hence the high thermal stability of nanostructured materials is observed. The temperature  $T_{\text{transition}}$  is unequal for the structures with different grain size. For a very small grain size, e.g. nanostructured material, the  $T_{\text{transition}}$  is comparatively high,  $T_{\text{transition}} > T_{\text{melting}}$ . It was concluded that in the temperature range studied the grain growth kinetics is determined by triple junctions dragging force.

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## **Grain-Boundary-Induced Nucleation of HCP-Martensite**

Mikhail Yu. Gutkin<sup>1</sup>, Kristina N. Mikaelyan<sup>1</sup>, and Victor E. Verijenko<sup>2</sup>

<sup>1</sup>*Institute of Problems of Mechanical Engineering, Russian Academy of Sciences,  
Bolshoj 61, Vasil. Ostrov, St. Petersburg 199178, Russia.*

<sup>2</sup>*School of Mechanical Engineering, University of Natal, Durban 4041, South Africa*

Martensitic FCC→HCP phase transformation has extensively investigated during last 70 years. The mechanisms and conditions of its realization have been studied by many authors on various materials as Co- and Fe-based alloys, and steels. In recent years, the special attention has been paid to this martensitic transformation (MT) for its key role in shape memory, damping and orthopedic implant alloys. On the other hand, the FCC→HCP MT represents the simplest case among other MTs and may be considered as a good model example for better understanding the nature and properties of MTs. However, the number of appropriate theoretical models looks quite limited. Olson and Cohen [1] done the most clear and comprehensive theoretical consideration of the initial steps of MTs. They proposed the model of heterogeneous embryo nucleation at that site of a grain boundary where exist some extrinsic dislocations. The model [1] describes well both the geometry and thermodynamics of the spontaneous nucleation of a martensitic embryo. However, the authors did not investigate in detail the elastic stresses of the embryo and its growth under external stress that would be especially important for applications. Moreover, they did not take into consideration the energy terms caused by interactions of the dislocations with remained defect arrangements at the grain boundary and with each other.

We propose an approach similar to that in [1] but with a more detailed account for elastic fields and energetics of the grain-boundary-martensitic-embryo system. A dislocation-disclination model is developed describing heterogeneous nucleation of an embryo of HCP-martensite at a tilt grain boundary segment containing some extrinsic dislocations. The total energy gain due to HCP-embryo nucleation is analysed in detail and the existence of both the equilibrium and critical embryo sizes under some external conditions, temperature and shear stress, is shown. Depending on the external conditions, these characteristic embryo sizes may vary in wide ranges. So, the equilibrium (critical) size increases (decreases) as the external shear stress increases and the temperature decreases. It is also demonstrated that a critical external stress exists which induces athermal embryo nucleation when the nucleation energy barrier disappears and the terms of equilibrium and critical embryo sizes lose their significance. The critical external stress has been studied depending on the temperature and characteristic parameters of the grain boundary where the FCC→HCP MT takes place. It occurs, in particular, that the critical external stress increases in direct proportion with both the grain boundary misorientation angle and temperature. We believe that the proposed model may serve as a basis for further investigations of the role of grain boundaries in accelerating or hampering MTs.

[1] G.B.Olson and M.Cohen, Metall. Trans. A7 (1976) 1897.

## **Effect of Free Surface on Heterogeneous Martensite Nucleation**

Mikhail Yu. Gutkin<sup>1</sup>, Kristina N. Mikaelyan<sup>1</sup>, and Victor E. Verijenko<sup>2</sup>

<sup>1</sup>*Institute of Problems of Mechanical Engineering, Russian Academy of Sciences,  
Bolshoj 61, Vasil. Ostrov, St. Petersburg 199178, Russia.*

<sup>2</sup>*School of Mechanical Engineering, University of Natal, Durban 4041, South Africa*

It is well documented that martensitic transformations (MTs) may go in different ways in bulk materials and thin foils or particles. In the latter case, the number of appropriate sites for martensite nucleation and the temperature gradients (and therefore thermo-elastic stresses) diminish that hamper development of martensite structures. On the other hand, the presence of free surfaces must decrease energy barriers related to martensite embryo generation. In considering MTs of a massive pre-strained sample, one should take into account that the material areas near free surfaces are commonly deformed much more than those in the bulk because the free surfaces serve as sources for dislocations and other defects. Therefore, the number of nucleation sites must increase from bulk to surface. This factor as well as the screening effect of free surfaces on the elastic fields and energies of defects which realise martensite nucleation and growth, allow one to expect that MT must start near free surfaces in a massive sample. Of course, such surface defects like microcracks, scratches, steps, etc., being stress concentrators, will also provide martensite nucleation near free surfaces. Despite the apparent importance of the role of free surfaces in MTs, there is a lack of appropriate theoretical models. The only work known to the authors is the paper [1] where surface nucleation of martensite under a localized normal stress using a simple dislocation model were considered. This model was elaborated rather to demonstrate heterogeneous MT under short-range elastic contact stresses and may hardly be applied to study the role of free surface itself.

We propose a dislocation-disclination model which describes heterogeneous nucleation of an embryo of HCP-martensite near a free surface at a tilt grain boundary segment containing some extrinsic dislocations. The total energy gain due to the HCP-embryo nucleation is calculated and analysed in detail with an exact account for the screening effect of the free surface. It is shown that the main characteristics of the HCP-martensite embryo nucleation (the energy barrier and critical size) depend strongly on the distance from the free surface. In fact, the distance from the free surface, together with the orientation angle of the grain boundary where the nucleation occurs, temperature and external shear stress, determines either the nucleation has a spontaneous barrier-less character or not. The distance from the free surface which separates these two regimes of martensite nucleation is called here as critical one. This critical distance decreases with the temperature and orientation angle, while it increases with the external shear stress. At low-level stresses, the critical distance is small enough (of order of some embryo thicknesses) while at high-level stress, it may tend to infinity. In the first case, the barrier-less martensite nucleation occurs within a thin sub-surface layer of the sample. In the second case, the whole section of the sample is subjected to the spontaneous barrier-less nucleation.

[1] I.-W. Chen and Y.-H. Chiao, *Acta Metall.* 33 (1985) 1827.

## Grain Boundary Channel Formation during Interdiffusion in Alloys

Lyudmila N. Paritskaya<sup>1</sup>, Valeri V. Bogdanov<sup>1</sup>, Yuri Kaganovskii<sup>2</sup>, Wolfgang Gust<sup>3</sup>

<sup>1</sup>*Department of Crystal Physics, Karazin National University, Kharkov, Ukraine*

<sup>2</sup>*Department of Physics, Bar-Ilan University, Ramat-Gan, Israel*

<sup>3</sup>*Institut für Metallkunde der Universität Stuttgart, Germany*

We present results of an experimental study of a new phenomenon accompanying grain boundary (GB) interdiffusion: the hole channel formation along GBs. The objects for study were plates of a homogeneous Cu-5 at.% Sn alloy, which were annealed at 800°C in purified hydrogen. The evolution of microstructure and the concentration distribution in the subsurface layers after successive stages of annealing were examined by an optical and scanning electron microscope, provided with X-ray microanalysis. Porous zones were found with GB hole channels perpendicular to the surface and practically equidistant from one another. The porous zone propagation and the average pore size growth at early stages of annealing obey a parabolic law. The observed processes are caused by nucleation and growth of the  $\text{Cu}_3\text{Sn}$  phase at the free surface. The new phase works as “diffusion pump” pumping out Sn atoms from the alloy toward the growing compound layer. At the later stages of annealing the GB channels elongated, but the porous zone propagation and the pore size growth are retarded and deviated from the parabolic law. Diffusion of Ni atoms from the “independent” source located on the free surface activates these processes by formation of a new  $(\text{NiCu})_3\text{Sn}$  phase.

GB channel formation has been described as a relaxation process accompanying GB interdiffusion of Sn and Cu atoms with unequal partial diffusion coefficients ( $D_{\text{Sn}} > D_{\text{Cu}}$ ). Excessive vacancies appearing at the GBs due to inequality between  $D_{\text{Sn}}$  and  $D_{\text{Cu}}$  are absorbed by bulk and GB sinks, and tensile stresses appear near the GBs stimulating hole channels or groove formation. A proposed model of GB channel and pore zone formation has been confirmed by evaluation of  $D_{\text{Sn}}$ ,  $D_{\text{Cu}}$ , and vacancy supersaturation from the parabolic growth laws, as well as from experimental results on interdiffusion in three-layer samples Cu-5 at.% Sn / Cu / Cu-5 at.% Sn with inert markers. Tensile stresses estimated from the GB channel geometry are of the same order of magnitude that are known for diffusion stresses.

## Interdiffusion and Accompanying Effects in Binary Nano-Structures

Lyudmila N. Paritskaya<sup>1</sup>, Valeri V. Bogdanov<sup>1</sup>, and Yuri Kaganovskii<sup>2</sup>

<sup>1</sup>*Department of Crystal Physics, Karazin National University, Kharkov, Ukraine.*

<sup>2</sup>*Department of Physics, Bar-Ilan University, Ramat-Gan, Israel*

Interdiffusion and diffusion homogenization were studied using three types of samples: 1) two-layer diffusion couples of contacting Cu and Ni layers compacted from nano-powders; 2) powder compacts of 50:50% Cu-Ni and Cr-Ni mixtures; 3) multilayer objects with alternating Cr and Ni layers, obtained by mechanical alloying. The grain size in the samples varied between 8 - 12 nm. The samples were isothermally annealed in the temperature range  $(0.3-0.5)T_m$ , where  $T_m$  is the melting temperature of the forming solid solution's base component. At each successive stage of isothermal annealing, the evolution of microstructures, concentration distributions and phase compositions were examined by the methods of optical and scanning electron microscopy with X-ray microanalysis, and X-ray phase analysis.

The developed network of grain boundaries (GBs) and interfaces exhibited the “non-classical” diffusional behavior of these objects. It was detected that at early stages of interdiffusion, with  $t < a^2/D_v$  (here  $D_v$  is the bulk interdiffusion coefficient, and  $a$  is the lattice parameter), the formation of a solid solution occurs in such systems without any participation of bulk diffusion. The obtained results have been interpreted in terms of diffusion along GBs (moving due to recrystallization), accompanied by the bulk's capture of the diffusant after GB displacement. For this model we have estimated the triple product  $P = kD_b\delta_b$  for moving boundaries ( $k$  is the GB adsorption coefficient,  $D_b$  is the GB diffusion coefficient and  $\delta_b$  is the effective GB width) using our experimental data on the recrystallization rates and solution concentrations. The obtained values of  $P$  for moving boundaries turned out to be virtually equal to the literature data for stationary GBs. Criteria for low-temperature homogenization (LTH) have been formulated.

It has been found that LTH by moving GBs and interfaces in multi-layer objects is accompanied by decay of the layered structure, caused by a chemical driving force, which according to our estimates, exceeds the capillary driving force. The mechanisms of this new phenomenon – diffusion-induced decay of layer structures – are discussed founding on experimental data for the multi-layer Cr-Ni system.

Interdiffusion in nanostructures is accompanied by the “boundary” Kirkendall effect, which was measured using the developed network of GBs. It confirms the inequality of partial diffusion coefficients along GBs during interdiffusion. The Kirkendall shift for the boundary Kirkendall effect is proportional to  $t^{3/4}$ , differing from the known parabolic kinetic law for the bulk Kirkendall effect.

## Transformation of Slip Dislocations in $\Sigma 3$ Grain Boundary

Juliana Gemperlová<sup>1</sup>, Alain Jacques<sup>2</sup>, Antonín Gemperle<sup>1</sup>, Niva Zárubová<sup>1</sup>

<sup>1</sup> *Institute of Physics AS CR, Na Slovance 2, 182 21 Praha 8, Czech Republic*

<sup>2</sup> *LPM, Ecole des Mines, parc de Saurupt, 54042 Nancy Cedex, France*

*In situ* straining experiments have been performed on symmetric  $\Sigma 3$  Fe-5.5at%Si bicrystals to elucidate the role of the grain boundaries (GB) in the slip propagation process. In bulk samples studied by X-ray diffraction topography, wide slip bands formed in one of the grains before propagating to the other. Stress accumulation at the heads of the slip bands was observed even in the case of  $\Sigma 3$  bicrystals with  $(\bar{1}12)_A$  GB plane and the primary slip system common to both grains. In this case (Burgers vector lying in the GB plane) no image forces are present and no interaction of slip dislocations with GB dislocations (GBDs) is possible. Since no insight into the creation of the stresses could be gained by X-ray topography, TEM was used for further study. *In situ* TEM straining was performed and conventional TEM was applied on foils prepared from selected areas of the samples previously investigated by X-ray topography.

Tensile samples were prepared with the GB touching a small hole in the centre of the platelet and parallel to the tensile axis.  $\frac{a}{2}[\bar{1}11]_A = \frac{a}{2}[1\bar{1}1]_B$ ,  $(110)_{A,B}$  was the primary slip system. During straining the two sides of the hole exhibited different behaviour due to a non-uniform distribution of stresses around it. On one side slip dislocations of the common slip system moved in nearly parallel slip planes farther from the GB. They were trapped in the GB, exerted repulsive stresses on the incoming dislocations and strongly deviated their slip planes. The images of the trapped dislocations are diffuse in contrast to sharp ones of GBDs. Until the end of straining no dislocations moved off the boundary. On the other side of the hole a different slip system with Burgers vector  $\frac{a}{2}[111]_B = \frac{a}{6}[511]_A$  was activated in grain B. Its dislocations entered the boundary and after a certain increase of strain some of them decomposed according to  $\frac{1}{6}[511]_A = \frac{1}{6}[333]_A + \frac{1}{6}[222]_A$  into a  $\frac{1}{2}[111]_A$  slip dislocation and a  $\frac{1}{2}[\bar{1}\bar{1}\bar{1}]_A$  residual dislocation. The decomposition needs additional energy. The slip dislocations in grain A moved out of the boundary leaving residual dislocations in it. Foils for conventional TEM were prepared from a specimen with very low additional deviation (tilt and twist components of the order of  $0.1^\circ$ ). Areas free of slip dislocations and areas of isolated slip bands of the common slip systems were observed. It followed from the comparison of corresponding images that inside the boundary the slip dislocations dissociate into three DSC dislocations:  $\frac{a}{2}[\bar{1}11]_A = \frac{a}{6}[\bar{1}11]_A + \frac{a}{6}[\bar{1}11]_A + \frac{a}{6}[\bar{1}11]_A$ . The driving force of the dissociation is a high reduction of the energy. The trapped dissociated dislocations create long-range stresses that contribute to the accumulation of dislocations at the boundary. Stress increase during further straining leads to recombination of the three DSC dislocations into one slip dislocation and to its movement out of the boundary. In both observed cases the governing mechanism of slip propagation is a transformation of the incoming slip dislocation in the boundary necessitating a stress increase.

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## Refined Prediction of Dislocation Structures in Low $\Sigma$ Symmetric Grain Boundaries

Antonín Gemperle, Juliana Gemperlová, Niva Zárubová

*Institute of Physics AS CR, Na Slovance 2, 182 21 Praha 8, Czech Republic*

In [1] a procedure was outlined for prediction of grain boundary dislocation (GBD) structures of symmetric *bcc* and *fcc* bicrystals from  $\Sigma 3$  to  $\Sigma 11$ . The prediction was based on experimentally determined misorientation and analogies between DSC vector configurations with respect to GB planes. A preference for two structure types was supposed. The first type contains a hexagonal net formed by pure or mainly screw dislocations and a set of parallel edge dislocations, the second type a hexagonal net formed by one edge and two mainly screw dislocations and a set of parallel screw dislocations. Only basic DSC vectors were considered. In a few cases e.g.  $\Sigma 5$  [001] (310)<sub>A</sub> the structure could not be designed on this basis.

In this contribution various published methods of DSC vector calculations are critically compared. It is stressed that only Burgers vectors of the same type in both grains are real GBD vectors. The structure predicted for *bcc*  $\Sigma 11$  [101] (32 $\bar{3}$ )<sub>A</sub> is verified on a Mo bicrystal. The uncertain case of *bcc*  $\Sigma 5$  [001] (310)<sub>A</sub> is experimentally investigated. In this bicrystal no one of the basic DSC vectors  $\frac{1}{5}[2\bar{1}0]_A$ ,  $\frac{1}{5}[120]_A$ ,  $\frac{1}{10}[315]_A$ ,  $\frac{1}{10}[1\bar{3}5]_A$  has strong preference for edge orientation with respect to the (310)<sub>A</sub> plane. A Fe-4at%Si bicrystal was prepared with about 2° mainly tilt deviation from the exact coincidence. A thin hexagonal net and a dense system of parallel dislocations were observed by TEM. Contrast analysis in various reflections and comparison of geometrical analysis of the structure with deviation measured by Kikuchi line technique revealed that the parallel set is formed by edge dislocations  $\frac{1}{5}[310]_A = \frac{1}{5}[2\bar{1}0]_A + \frac{1}{5}[120]_A$ . The hexagonal net is composed of screw dislocations  $\frac{1}{10}[1\bar{3}5]_A$ ,  $\frac{1}{10}[\bar{1}35]_A$  and  $\frac{1}{5}[\bar{1}30]_A = \frac{1}{5}[120]_A + \frac{1}{5}[\bar{2}10]_A$ .

It is concluded that in unfavorable cases even combinations of the three smallest DSC vectors exist as GBD vectors. Using this new result the table of predicted GBD structures for  $\Sigma 3$  to  $\Sigma 11$  was redesigned.

[1] A. Gemperle, T. Vystavel and J. Gemperlová, Mat. Sci. Forum **294-296** (1999) 393.

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## **Interfacial Fatigue Cracking in Copper Bicrystals with Different Geometrical Relationships between Grain Boundary and Slip Systems**

Y.Kaneko<sup>1</sup>, Y.Yamaguchi<sup>2</sup>, H.Miyamoto<sup>2</sup>, T.Mimaki<sup>2</sup> and S.Hashimoto<sup>1</sup>

<sup>1</sup>*Department of Intelligent Materials Engineering, Faculty of Engineering,  
Osaka City University, Osaka 558-8585, Japan.*

<sup>2</sup>*Department of Mechanical Systems Engineering, Faculty of Engineering,  
Doshisha University, Kyotanabe, Kyoto, Japan.*

Fatigue crack initiation and propagation have been investigated in copper bicrystals having tilt boundaries, from a viewpoint of geometrical relationship between a grain boundary and slip systems. Five copper bicrystals of different orientation relations were grown by the Bridgman method using seed crystals, from a material of 99.9999% purity. Constituent grains of the bicrystals were oriented to be single slip. Schmid factors of adjoining grains were controlled to be same. In order to observe slip steps, the primary slip vectors were directed between tensile axis and top surface axis, thus side surface of all the constituent grains were  $\{111\}$  cross slip planes. Consequently, the grain boundaries of the bicrystals were  $\langle 111 \rangle$  asymmetrical tilt boundaries. Disorientation angles  $\theta$  were analyzed to be  $\theta=13.2^\circ$ ,  $15.8^\circ$ ,  $47.2^\circ$ ,  $52.9^\circ$  and  $58.9^\circ$ , respectively. The bicrystal specimen of  $\theta=13.2^\circ$  has the orientation relationship of  $\Sigma 3$  and the boundary plane of (110).

Cyclic deformation tests were carried out in air at room temperature. During cyclic deformation test, a plastic shear strain amplitude was kept constant at  $\gamma_{pl} = 2 \times 10^{-3}$ . Cyclic frequency of triangular strain wave was 0.5Hz. From the beginning of the cyclic deformation tests, the stress amplitude increased rapidly with increasing cycles and then saturated, as usually observed in cyclic deformation tests of copper single crystals. There were no significant differences in cyclic hardening behavior among the bicrystals. In this sense, the character of the grain boundary had little influence on the cyclic hardening of the bicrystals.

The cyclic deformation tests were interrupted when stress amplitude decreased rapidly due to formations of fatigue cracks. Modes of fatigue cracking were different among the bicrystals. In the bicrystals of  $\theta=13.2^\circ$ ,  $15.8^\circ$  and  $58.9^\circ$ , the fatigue cracks were initiated within the constituent grains. No intergranular fatigue cracks were detected. On the other hand, the intergranular fatigue cracks were nucleated and propagated in the bicrystals of  $\theta=47.2^\circ$  and  $52.9^\circ$ . The geometrical relationship between the grain boundary and the slip systems of the constituent grains could be classified into two kinds (Types A and B geometry). Type A geometry has the primary slip planes which are almost parallel to each other. Type B geometry has the primary planes which are located symmetrically with respect to the grain boundary plane. In the bicrystals having Type A geometry, no intergranular cracks were detected. The intergranular cracks were always observed at Type B geometry. However, the bicrystal of  $\theta=58.9^\circ$  showed no intergranular cracks in spite of Type B geometry. Because the orientation relation of the  $\theta=58.9^\circ$  bicrystal was  $\Sigma 3(110)$  twist boundary, the structure of grain boundary could affect the absence of the intergranular fatigue cracking.

## **Cyclic Deformation under Several Plastic Strain Amplitudes in Pb-62%Sn Eutectic Alloy processed by ECAP method**

Y.Kaneko, Y.Inoue and S.Hashimoto

*Department of Intelligent Materials Engineering, Faculty of Engineering,  
Osaka City University, Osaka 558-8585, Japan.*

Cyclic deformation properties of Pb-62%Sn eutectic alloy processed by equal channel angular pressing (ECAP) have been investigated. Recently, grain refinement by the ECAP method has extensively been examined in several metallic materials and excellent improvements of strength were reported. This kind of the grain refinement also leads to the increasing area of grain boundary. Consequently, the plasticity is also improved in the alloys of low-melting point, which is processed by the ECAP method. This improvement can be attributed to the increase in grain boundary sliding. In many cases, superplasticity is observed at higher temperatures. However, cyclic deformation tests demanding both precise control and measurement is difficult to perform at such high temperature. The above alloy having high plasticity is convenient to perform fatigue test at room temperature.

As-melted bulks of 20mm diameter passed through the ECAP processing for one time (Specimen 1-pass) and three times (Specimen 3-passes). The as-melted bulk is also shaped to the specimen (Specimen as-melt). Average grain sizes of Specimens 1-pass, 3-pass and as-melt were 2.4 $\mu\text{m}$ , 2.5 $\mu\text{m}$ , 5.0 $\mu\text{m}$ , respectively. These materials were shaped to strip specimens having a square gauge shape of 3 $\times$ 3.5mm<sup>2</sup> and gauge length of 6mm. Monotonic tensile deformation tests were carried out at room temperature at an initial strain rate of 1.0 $\times 10^{-3}$  s<sup>-1</sup>. Cyclic deformation tests were done also at room temperature. A total strain rate of the cyclic tests was 1.0 $\times 10^{-3}$  s<sup>-1</sup>. Plastic strain amplitudes  $\epsilon_{pl}$  were controlled to be constant values of 1 $\times 10^{-4}$ , 3 $\times 10^{-4}$ , 1 $\times 10^{-3}$  and 3 $\times 10^{-3}$ .

Monotonic tensile deformation behaviour was significantly different among three kinds of the specimens. The strains at fracture in Specimens as-melt, 1-pass and 3-passes were approximately 80%, 210% and 300%, respectively. It was found that the Pb-Sn alloy processed by the ECAP possessed high plasticity even at room temperature. Flow stress during tensile deformation depended on the processing. Ultimate tensile strengths were 44MPa, 33MPa and 24MPa for Specimens as-melt, 1-pass and 3-passes, respectively. The stress amplitudes during cyclic deformation tests were almost constant, except for the plastic strain amplitude of 3 $\times 10^{-3}$  where the stress amplitude decreased gradually with increasing cycles. The maximum stress amplitudes during cyclic tests increased with the increasing strain amplitude for all the materials. The as-melted samples showed the highest stress amplitude among three materials. However, the stress amplitudes of Specimen 1-pass and 3-passes were almost same. This result is difficult to be interpreted by the flow stresses obtained in the monotonic tensile tests.

From the surface observation after cyclic deformation test, grain boundary and phase boundary sliding occurred in some specimens. At the low strain amplitude ( $\epsilon_{pl} = 1 \times 10^{-4}$  and 3 $\times 10^{-4}$ ), the grain boundary sliding was difficult to be recognized in Specimen as-melt. When the plastic strain amplitude was raised to 1 $\times 10^{-3}$ , the sliding steps could be detected at several grain boundaries. In the specimens processed by the ECAP method, the boundary steps were observed at all the plastic strain amplitudes tested. Fatigue cracks were nucleated at such grain boundary steps.

## Deflection of Fatigue Cracks in The Vicinity of Grain Boundaries in Copper Bicrystals

<sup>1</sup>Y.Kaneko, <sup>2</sup>K.Kitagawa and <sup>1</sup>S.Hashimoto

<sup>1</sup>*Department of Intelligent Materials Engineering, Faculty of Engineering,  
Osaka City University, Osaka 558-8585, Japan.*

<sup>2</sup>*Department of Mechanical Systems Engineering, Faculty of Engineering,  
Kanazawa University, Kanazawa 920-8667, Japan.*

The purpose of the present study is to investigate deflections of intragranular fatigue cracks, which is caused by the presence of grain boundaries. Changes in the crack paths have been examined when intragranular fatigue cracks approached the grain boundaries.

A single crystal and bicrystals of three kinds (Bicrystals A, B and C) were grown by the Bridgman method. These crystals were shaped to single-edge-notched specimens. The grain boundaries located in between Grain I and II of the bicrystals were inclined to tensile axis at about 35°. The notch of the bicrystal was introduced in Grain I. The tensile and surface axes of the single crystal specimen were oriented to be [001] and [110] directions, respectively. Because the tensile axis is the [001] direction, four {111} slip planes are equivalently sheared. For all the bicrystal specimen, the crystallographic orientation of Grain I having the notch is equal to that of the single crystal specimen. One of the {111} slip planes in Grain I was parallel to the grain boundary plane. On the other hand, orientations of Grain II were different among Bicrystals A, B and C. The primary slip plane of Grain II was parallel to the grain boundary plane in Bicrystal A. These constituent grains have the orientation relationship of the  $\Sigma 3(111)$  coherent twin. The primary plane of Grain II in Bicrystal B is common to one of the slip planes in Grain I. It is expected that dislocation can traverse the grain boundary along these two planes. The primary plane of Grain II in Bicrystal C had no special relations to the grain boundary and slip systems in Grain I. The fatigue crack growth tests were carried out in air at room temperature in a servo-hydraulic machine. Load ratio ( $=P_{\min}/P_{\max}$ ) was set at -0.5. The stress amplitude was raised stepwise until the growth of the fatigue crack was detected.

In the single crystal specimen, a fatigue crack nucleated at the notch tip started to propagate towards notch direction that is perpendicular to the tensile axis. It was noticed that  $(1\bar{1}1)$  and  $(1\bar{1}\bar{1})$  slip planes were operated in the upper and lower sides of cracked matrices, respectively. Accordingly, it is likely that the observed fatigue crack perpendicular to the tensile axis was grown by means of the symmetric operation of the  $(1\bar{1}1)$  and  $(1\bar{1}\bar{1})$  slip planes around the crack tip. A fatigue crack in Bicrystal A was deflected, unlike the single crystal specimen. Especially in the vicinity of the grain boundary, the fatigue crack propagated almost parallel to the grain boundary plane. One of two slip planes contributing to the intragranular crack propagation should be restricted by the grain boundary. It is feasible that the fatigue crack propagated along the other operative slip plane by the manner of shear decohesion. A fatigue cracks in Bicrystal B was also inclined to the notch direction. This deflection is difficult to understand from a viewpoint of slip continuity across the boundary plane. This can be interpreted by an additional shear stress coming from the elastic incompatibility of the constituent grains.

In Bicrystal C, the mode of fatigue cracking in Grain I was changed due to the presence of Grain II. The fatigue crack was grown along the slip plane which has good plastic compatibility with the primary system of Grain II.

## **Investigation of the Strain Relaxation Mechanism in the Si-SiO<sub>2</sub> System during the Process of its Formation**

D.Kropman<sup>1</sup>, V.Poll<sup>1</sup>, T.Kärner<sup>2</sup>, Ü.Ugaste<sup>3</sup>, E.Mellikov<sup>4</sup>, U.Abru<sup>5</sup>

<sup>1</sup>*Estonian Maritime Academy, Mustakivi 25, 13912 Tallinn, Estonia.*

<sup>2</sup>*Institute of Physics, Tartu University, Tartu, Estonia.*

<sup>3</sup>*Pedagogical University Tallinn, Estonia.*

<sup>4</sup>*Technical University, Tallinn, Estonia.*

<sup>5</sup>*Tondi Electronics, Tallinn, Estonia.*

It is well known that internal mechanical stresses due with the differences in the thermal expansion coefficient between films and substrates and lattice mismatch appear in the Si-SiO<sub>2</sub> system during the process of its formation and that point defects generation and redistribution reduce partially the surface strain. However, no investigation of this process on the atomic scale has been carried out so far.

The purpose of the present work is to investigate the strain relaxation mechanism in the Si-SiO<sub>2</sub> system by means of EPR, IR absorption spectroscopy and samples bending measurements.

It has been found that in the case of lower oxidation temperature (1100° C) the bending of the samples decreases with the increase of the point defects density (E' centres in SiO<sub>2</sub> and vacancies complexes in Si) while at higher oxidation temperature (1200° C) the bending of the samples and point defects density increase simultaneously. In the first case it may be due to the relaxation of strain by generation of point defects, in the second one, by creation of point defects and broken bonds by the stresses.

To separate the stresses in the SiO<sub>2</sub> from the stresses in Si surface region the interdependence between E' centres EPR signal intensity and the linewidth of SiO<sub>2</sub> IR absorption at 1100 cm<sup>-1</sup> ( $\Delta\nu$ ) were investigated [1]. It has been established that depending on the oxidation condition E' centres density and  $\Delta\nu$  increases or decreases simultaneously. This interdependence may be explained by creation of repulsive forces between positively charged E' centres that bring about increase of the stresses, and consequently  $\Delta\nu$ , in the SiO<sub>2</sub> film.

The obtained results confirm that there exists an interdependence between the strain relaxation mechanism in Si-SiO<sub>2</sub> structure and point defects in Si and SiO<sub>2</sub>. The strain and stresses in the Si-SiO<sub>2</sub> systems may be reduced by appropriate choice of the oxidation condition and postoxidation treatment.

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## **Intergranular Corrosion and Stress Corrosion Cracking of Pure Copper <111> Tilt Bicrystals**

Hiroyuki Miyamoto<sup>1</sup>, Hirohito Koga<sup>1</sup>, Takuro Mimaki<sup>1</sup> and Satoshi Hashimoto<sup>2</sup>

<sup>1</sup> *Department of Mechanical Engineering, Faculty of Engineering, Doshisha University, Kyoto, Japan,* <sup>2</sup> *Department of Intelligent Materials, Faculty of Engineering, Osaka City University, Osaka, Japan.*

Behaviour of intergranular corrosion and stress corrosion cracking (SCC) in a series of pure copper bicrystals with symmetrical [111]-tilt boundaries were investigated. For corrosion tests, a specimen was immersed in a naturally aerated solution of Livingston etchant, while, for SCC tests, a specimen having a notch at the grain boundary perpendicular to load axis was tensioned by slow strain rate technique (SSRT) in 1N NaNO<sub>2</sub> solution. Grain boundaries (GBs) were preferentially attacked in the solution in all bicrystals tested. The depth of intergranular grooves was dependent on the misorientation between two component crystals. When the depths of grooves were expressed as a function of misorientation angles, they show sharp minima at 38.1 and 58.1 degrees, which deviate slightly from  $\Sigma 7(321)$  and  $\Sigma 3(211)$  relation respectively. Wang et al predicted GB energy cusps at misorientation of  $\Sigma 7(321)$  and  $\Sigma 3(211)$ . Thus, the sensitivity of intergranular corrosion of [111] tilt GBs is strongly dependent on the GBs energy as reported by Yamashita on pure copper [110] tilt bicrystals [1].

The behaviour of SCC was generally different between small- and large-angle bicrystals. The small-angle bicrystals fractured in both intergranular and transgranular manners accompanied by a large amount of plastic strain to fracture. On the other hand, the large-angle bicrystals fractured in almost intergranular manner accompanied by the small plastic strain compared to those of the small-angle boundaries. Sensitivity of SCC, which was evaluated quantitatively in terms of the ratio of total strain energy to fracture in NaNO<sub>2</sub> solution to that in air, increase with increasing misorientation and becomes relatively constant in high-angle GBs. Although small cusps appeared at 38.1 and 58.1 degrees when SCC sensitivity were expressed as a function of misorientation, they were shallow compared to those appeared in the intergranular corrosion. Low sensitivity of small-angle GBs and relatively constant sensitivity irrespective of misorientation of large-angle GBs are consistent with the result of [110] tilt pure copper bicrystals reported by Mimaki et al [2]. Yamashita et al [3] examined misorientation dependence of SCC sensitivity for Cu-9at%Al alloy bicrystals and clarified that the sharp cusps which appeared at misorientations with low interfacial energy became less noticeable under higher applied stress. Local stress concentration at large-angle grain boundaries is high compared to that at small-angle GBs due to dislocations trapped at boundaries. Thus, it is considered that, under dynamic straining or higher applied stress, the effect of misorientation rather than GB energy becomes predominant on the SCC sensitivity.

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[2] T. Mimaki, M. Yamashita, S. Hashimoto and S. Miura; *Proc. 6<sup>th</sup> Int. Conf. on Mechanical Behaviour Materials*—, Kyoto, ed. M. Jono and T. Inoue, Pergamon press, (1991) 663.

[3] M. Yamashita, T. Mimaki, S. Hashimoto and S. Miura, *Phil. Mag.*, A 63 (1991) 707.

## **Misorientation Dependence of Energies of Si (001) Twist Grain Boundaries**

Akira Otsuki

*Institute of Advanced Energy, Kyoto University  
Gokasyo, Uji city, Kyoto, 611-0011, Japan*

The energies of Si(001) twist boundaries have been measured relative to the Si(solid)-Sn(liquid) interfacial energy by the dihedral angle method at 1473 K. The results are summarized as follows :

1. The existence of narrow(less than  $1^\circ$ ) and shallow energy cusps at the csl-misorientations corresponding to the low  $\Sigma$  boundaries of 5, 13, 17, 25, 37, 41 were found.
2. In addition, the existence of wide( $3-4^\circ$ ) and shallow energy cusps at misorientations of  $5.2^\circ$ ,  $8.8^\circ$ ,  $22.6^\circ$  and  $39.9^\circ$  were found. These misorientations were not correspond to low  $\Sigma$  boundaries except  $\Sigma=13(\theta=22.3^\circ)$ .
3. The energies of general boundaries discontinuously varied with misorientation angles across the misorientations observed the wide cusps, and these misorientations divided the misorientation regions of  $0^\circ$  to  $45^\circ$  for (001) twist boundaries with respect to the energies into 5 regions.
4. The boundaries observed the wide cusps seem to regard as delimiting boundaries which boundary structures alter with misorientations.
5. These wide cusps were found at the corresponding misorientations dividing, into 1:1 or 1:2, misorientation differences between each  $\Sigma=1, 25, 17, 5$  and 29 coincidence boundary.
6. The energies at regions between the wide cusps seem to refer to common structure units based on structures constructing low  $\Sigma$  boundaries of  $\Sigma=1, 25, 17, 5$  and 29.

## **The Interface Structure & External Field Influence on the Magnetic Properties of $\text{SmCo}_5$ , $\text{Nd}_2\text{Fe}_{14}\text{B}$ Permanent Magnets**

A.V.Andreeva<sup>1</sup>, N.M.Talijan<sup>2</sup>

<sup>1</sup>*Institute of Microelectronics Technology RAS, 142432 Chernogolovka, Moscow region, Russia.*

<sup>2</sup>*Institute of Chemistry, Technology and Metallurgy Njegoseva 12, PO Box 815, YU-11001, Belgrade, Yugoslavia.*

The influence of crystal texturing, interface structure and secondary phase precipitation on the magnetic properties of permanent magnets (PM) based on  $\text{SmCo}_5$  and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  high dispersion powders is investigated. The PMs based on powders of rare earth metals are nonequilibrium multiphase systems. The processes of structure selforganization giving rise to special crystallographic and magnetic textures are characteristic of these ultradisperse systems. The large influence of microstructure on the magnetic properties is determined by (a) distribution of secondary magnetically soft phases and nonmagnetic pores and oxides as boundary precipitates; (b) misaligned grains, interface structure and the type of coupling between the grains and (c) imperfect interfaces. Therefore, the role of intercrystalline interfaces formed during powder consolidation is very important.

The experimental data are discussed in terms of (1) generalised theory of interface and interfacial defect symmetry; (2) resonance principle of external field interactions and internal interface structure properties of the Sm-Co, Nd-Fe-B systems, arising from the selforganization process.

The experimental observations revealed

- the simultaneous increase in the rate of shrinkage and coercivity, as the Sm content in the alloy exceeds its stoichiometric amount in the  $\text{SmCo}_5$  phase;
- the influence of external magnetic field during powder consolidation process on the shrinkage and interface pore distribution;
- the definite crystallographic mutual orientation of the secondary phases as interface - precipitates and their influence on coercivity;
- the role of magnetocrystalline anisotropy and interface atomic structure in domain wall –grain boundary interactions, pinning and reverse domain nucleation mechanism in magnets with one easy magnetisation direction.

The optimised microstructures and alloy compositions of high – performance permanent magnets are proposed on the basis of experimental data and crystallographic analysis of the magnet texture. The phenomenon of high coercivity of permanent magnets has been treated in the framework of the theory of interfaces (calculations of the crystallographic parameters and atomic models of special coherent grain and phase boundaries in the Sm-Co and Nd-Fe-B systems), which affords some new insight in its origin. The application of the external field gradients (chemical and magnetic) as powerful tools for boundary engineering for high tech. permanent magnets based on ultradisperse  $\text{SmCo}_5$ ,  $\text{Nd}_2\text{Fe}_{14}\text{B}$  powders is discussed. .

## **The Problem of Structural Multiplicity of Interfaces in Bicrystals**

Victor P. Yashnikov

*Institute of Solid State Physics, Russian Academy of Sciences  
142432 Chernogolovka, Moscow District, Russia*

The classical calculus of variations approach operates with averaged characteristics of the interface in a bicrystal. Because the size of averaging is essentially greater than the related lattice parameters, this approach can not, in principle, to provide us with information about details of GB atomic structure. It is impossible, in particular, in the frame of the approach to predict the existence or to prove impossibility of the existence several structurally different interfaces having one and the same “seed” interface in an ideal bicrystalline structure. Mean time this is one of the most intriguing fundamental problems in of the interface science.

The paper is purposed to study of discrete analogs of extremal problems connected with the theory of interfaces in bicrystals. Ideal bicrystalline patterns and their dual Dirichlet-Voronoi partitions are considered. The notion of bicrystalline patterns is extended by adjoining topological bicrystals. Topological bicrystal generic to an ideal one is defined as pattern every point of which is obtained from a point of the ideal pattern by translation in the limits of the corresponding Dirichlet-Voronoi polyhedron.

After a choice and fixation of an appropriate cutoff domain the model conditions of tight binding on the external geometric boundary of the cutoff domain are taken. Further we introduce into consideration the global elastic distortion functional as the mean square distortion over all elementary atomic tetrahedrons belonging to a topological bicrystal. The distortion functional is correctly defined on the variety of all possible topological bicrystals whose interfaces have common board on the geometric external boundary of the chosen cutoff domain. It is demonstrated that the functional takes a value of the absolute minimum on the above mentioned variety. The condition of existence of several local minima are discussed. It is noted the possibility to use global distortion functionals based on more complicated orthogonal invariants of local homogeneous deformation than the sum of squares of eigenvalues.

It is observed that the relaxation process of a bicrystalline systems may be subdivided into two qualitatively different stages : 1.-The topological (or coarse) relaxation, i.e. the search of an ideal bicrystalline pattern whose topological class contains bicrystal with minimal value of the distortion functional; 2.-The metrical (or fine) relaxation in which the topological class of varying pattern leaves unchanged. We analyze in connection with that the possibility of existence of mean distortion minimal (i.e. relaxed) bicrystalline structures belonging to different topological classes. The conditions of existence of geometrically different relaxed bicrystalline systems to an one and same topological class are also discussed.

## **First Principles Computational Study of Sb Segregation to Twist Boundaries in ZnO**

H.S. Domingos and P.D. Bristowe

*Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, England.*

J. Carlson and B. Hellsing

*Experimental Physics, Chalmers and G utenborg University, SE-412 96 Gothenburg, Sweden.*

We have studied the atomic and electronic structure of two crystallographic variants of the  $\Sigma=7$   $21.8^\circ$  (0001) twist boundary in ZnO using first principles total energy pseudopotential calculations. The bonding characteristics of both structural variants are determined using a Mulliken population analysis. One of the structures is then doped with an Sb impurity and the changes in bonding and total energy of the doped boundary determined. The segregation energy is found to depend on the site chosen for Sb substitution with non-CSL sites strongly preferred. In preferred sites, the Sb impurity induces the formation of a new defect state which is located in the valence band. To determine the effect of further Sb segregation, we have incorporated by substitution a complete layer of Sb immediately adjacent to the boundary plane. With this additional segregation, we observe the formation of an impurity band located in the band gap region. Thus, impurity-impurity interactions have the effect of increasing the orbital energy of the single impurity defect state. In addition to changes in electronic structure, we find that the layer of Sb also distorts the atomic structure of the boundary so as to increase the local coordinations in an attempt, we believe, to form a layer of  $\text{Sb}_2\text{O}_3$ . The results are discussed in relation to the electrical properties of doped polycrystalline ZnO commonly used in varistors.

## Nanoscale Studies of the Chemistry of a René N6 Superalloy\*

Kevin E. Yoon<sup>1</sup>, Dieter Isheim<sup>1</sup>, Ronald D. Noebe<sup>2</sup> and David N. Seidman<sup>1</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208-3108 U.S.A.* <sup>2</sup>*NASA Glenn Research Center, Cleveland, Ohio 44135 U.S.A.*

Nickel-based superalloys are some of the most widely used high-temperature materials because they exhibit high corrosion and creep resistance at elevated temperatures. Through use of these materials, it is possible to increase the operating temperatures of turbine engines without the addition of cooling systems. Thus the need for improved Ni-based superalloys has been driven by the aerospace industry's demand for energy efficient turbine engines [1]. Single crystal Ni-based superalloys, with a  $\gamma/\gamma'$  microstructure, are being ameliorated constantly by modifying their chemistry and by processing improvements [2]. René N6 is a third generation commercial Ni-based superalloy, developed by General Electric, which contains the elements Ni, Co, Cr, Mo, W, Re, Al, Ta, and Hf. It is believed that the refractory alloying elements Ta, Re, W play important roles as solid-solution strengtheners that increase the strength of the  $\gamma$  (FCC) matrix. Adding Re increases the creep resistance, however the mechanism for the improved creep resistance has not been clarified.

Atom-probe field-ion microscopy (APFIM) is being used to study partitioning of the alloying elements between the  $\gamma$  (FCC) and  $\gamma'$  ( $L1_2$ ) phases and their segregation behavior at  $\gamma/\gamma'$  interfaces. The atomic-scale resolution and real space reconstruction capability for elemental mapping makes atom probe microscopy especially suitable for the subnanoscale investigation of multicomponent superalloys. Concentration profiles of René N6, obtained from an atom probe analysis, reveal the partitioning behavior of the alloying elements. As expected, the matrix strengtheners, such as Mo, W, and Re, are partitioned to the  $\gamma$  (FCC) matrix, but Re also exhibits significant enrichment at the  $\gamma/\gamma'$  interfaces. This agrees with a dynamical pile-up effect of Re in front of the moving interfaces of growing  $\gamma'$ -precipitates recently observed in the Ni-based superalloy RR3000 [3]. Segregation of Re at the  $\gamma/\gamma'$  interfaces increases the misfit between the matrix and the  $\gamma'$  precipitates and this delays the onset of creep at high temperature. While atom probe analyses of the alloy reveals the chemical nature of this alloy on a nanoscale, transmission electron microscopy studies are used to elucidate the microstructural relationships on a mesoscopic scale.

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## Vanadium Segregation at an Fe / Mo Heterophase Interface \*

Dieter Isheim<sup>1</sup>, Olof C. Hellman<sup>1</sup>, David N. Seidman<sup>1</sup>, Frédéric Danoix<sup>2</sup>, Alain Bostel<sup>2</sup> and Didier Blavette<sup>2</sup>

<sup>1</sup>*Department of Materials Science and Engineering, Northwestern University,  
2225 N. Campus Drive, Evanston, IL 60208-3108*

<sup>2</sup>*Groupe de Physique des Matériaux, UMR CNRS 6634, Faculté des Sciences de Rouen, F-  
76821 Mont Saint Aignan Cedex, France*

Upon aging, binary Fe-Mo alloys form a nanometer-scale modulated decomposition microstructure containing metastable Mo-rich precipitates [1], significantly increasing the hardness of the alloys [2]. Alloys with a Mo content replaced partially by vanadium produce a similar modulated decomposition structure [3]. The distribution of the constituents both among the evolving phases and at the heterophase interfaces between matrix and precipitates, however, remains undetermined.

The present research characterizes the phase formation and the local distribution of the constituents in an Fe-15 at.% Mo-5 at.% V alloy by both transmission electron and three-dimensional atom-probe microscopies. Special attention is given to the local composition at the heterophase interfaces. A method for evaluating the statistical significance of small-scale concentration fluctuations is developed.

This ternary alloy decomposes, in analogy to the binary alloy, by forming metastable BCC Mo-rich precipitates within the BCC Fe-rich matrix, while the equilibrium intermetallic phases are kinetically suppressed. The precipitate composition is Mo-13.0 at.% Fe-4.9 at.% V. With this result, the tie line of the metastable equilibrium between the decomposition products is at nearly a constant 5 at.% V concentration.

A vanadium enrichment of approximately 20 at.% is found in the interfacial region outside a Mo precipitate in a matrix region about 0.5 nm or 2-3 atomic layers thick. This corresponds to a Gibbsian interfacial excess of vanadium of  $3.3 \pm 1.3 \text{ nm}^{-2}$  or 0.2 *effective* monolayers.

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## **Channelling of Plastic Deformation by Interfaces in TiAl Intermetallics**

V. Paidar

*Institute of Physics, Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czech Republic*

The activity of possible deformation modes in the lamellar structure of Ti-rich TiAl alloys is governed by the asymmetry of motion of carriers of plastic deformation – superlattice dislocations and twinning, on one side, and by the direction of propagating deformation with respect to the lamellar interfaces, on the other side. The lamellae of different variants of the  $L1_0$  tetragonal phase are separated by special rotational interfaces on the  $\{111\}$  close packed planes. Their misorientation angle about the axis perpendicular to the lamellae is a multiple of  $60^\circ$ . Besides these special interfaces, general grain boundaries can also significantly influence the plastic deformation. While the effect of lamellar interfaces associated with their structure and properties is of mesoscopic nature, the boundaries between differently oriented lamellar colonies (between so called polysynthetically twinned crystals - PST), i.e. the grain boundaries in a common sense can also modify the stress distribution due to the compatibility stresses arising from the crystal elastic anisotropy and anisotropy of plastic deformation. Even in the case when the transfer of plastic deformation across the interfaces does not occur, the presence of interfaces as obstacles to moving dislocations and twins can lead to the localisation of strain parallel to the lamellae, so called channelling of deformation.

In this paper, first the microstructure of TiAl intermetallics and the character of different interfaces will be described, and then the effect of various interfaces on mechanical properties will be discussed.

## **The Influence of Microstructure in Electroless Deposited, Cobalt Based Thin Films on Diffusion Barrier Integrity in Copper Metallization**

Amit Kohn<sup>1</sup>, Moshe Eizenberg<sup>1</sup>, and Yosi Shacham-Diamand<sup>2</sup>

<sup>1</sup>*Department of Materials Engineering, Technion, Haifa, Israel*

<sup>2</sup>*Department of Physical Electronics, Tel-Aviv University, Ramat-Aviv, Israel*

The application of Cu metallization in ULSI devices requires the development of efficient ultra thin diffusion barriers. Electroless is a potential deposition method as it is a selective, low temperature process readily integrated with electrochemical copper deposition, which is the current Cu deposition method. In this research, we evaluate Co based thin films:  $\text{Co}_{0.9}\text{P}_{0.1}$ ,  $\text{Co}_{0.96}\text{W}_{0.04}$  and  $\text{Co}_{0.9}\text{P}_{0.08}\text{W}_{0.02}$ , as potential barriers against Cu diffusion.

In electroless deposition, reaction kinetics can be dominant, resulting in a nanocrystalline or amorphous structure of the metallic layer. This microstructure improves the quality of the diffusion barrier by eliminating direct, fast diffusion paths via the grain boundaries. For electroless Co, this modification of the microstructure is achieved by the incorporation of P and W. In the as-deposited films, nanocrystalline hcp Co grains were obtained. Additionally, under equilibrium conditions, the solubility of P and W in Co is by more than one order of magnitude lower than the amounts incorporated in the electroless deposited films. Therefore, we expect the impurities to enrich the Co grain boundaries after thermal treatment. After subjecting the films to thermal treatments up to 700°C, TEM and XRD studies revealed microstructural evolution of nucleation, crystallization of hcp Co, grain growth along a preferred basal plane orientation, formation of  $\text{Co}_2\text{P}$  precipitates and a delayed phase transformation from hcp to fcc Co.

The consequence of the diffusion barrier failure is the creation of Cu induced deep level traps in the forbidden band gap of the Si semiconductor, significantly reducing the minority carrier lifetime. The concentration of electrically active Cu, which can drastically alter the electrical characteristics of a microelectronic device, is  $10^9 - 10^{13} \text{ cm}^{-3}$ . The evaluation of diffusion barrier integrity in this research is based on electrical characterization of MOS devices.

In order to examine the role of the impurity type and composition in determining the diffusion barrier quality,  $\text{Co}_{0.9}\text{P}_{0.1}$  and  $\text{Co}_{0.96}\text{W}_{0.04}$  30 nm thick films, subjected to thermal stress at 450°C, were evaluated. The  $\text{Co}_{0.9}\text{P}_{0.1}$  diffusion barrier was stable for 8-12 hours, while  $\text{Co}_{0.96}\text{W}_{0.04}$  failed after less than 0.5 hour. Experimental microstructural observations indicate that the dominant diffusion of Cu in the thin films at 450°C is via the grain boundaries. The significant difference in the diffusion barrier quality between the two films is mainly attributed to the type and amount of impurities at the grain boundaries. Thermodynamic data shows that a Cu-P reaction is favorable unlike that of Cu-W. Consequently, the improved barrier properties of the  $\text{Co}_{0.9}\text{P}_{0.1}$  films may be explained by the “stuffing” mechanism. Phosphorus, enriching the grain boundaries, reacts with Cu, hindering its diffusion.

## **Analytical Electron Microscopy of the $\gamma'$ / $\gamma$ Interface in a Nickel-Base Superalloy**

Krzysztof Hodor <sup>1</sup>, Pawel Zieba <sup>1</sup>, Barbara Olszowska-Sobieraj <sup>2</sup>

*(1) Polish Academy of Sciences, Reymonta St. 25, 30-059 Cracow, Poland;*

*(2) Academy of Mining and Metallurgy, Reymonta St. 23, 30-059 Cracow, Poland*

Nickel-base superalloys are used for a range application in aircraft engines because of their excellent high temperature strength and oxidation resistance. The structure of the Ni-base superalloy is characterised by presence of cuboidal  $\text{Ni}_3\text{Al}$  precipitates of  $\gamma'$  phase within the  $\gamma$  matrix with face-centred cubic structure.

In this paper the investigation of microstructure and chemical composition of the  $\gamma$  and  $\gamma'$  phases were performed in Ni-base superalloy by means of analytical electron microscopy. The distribution of particular elements in the alloy was revealed using X-ray mapping EDAX Phoenix facility attached to the CM 20 Philips transmission electron microscope.

This allowed to determine the partition of alloying elements between  $\gamma'$  and  $\gamma$  phases as well as at the  $\gamma'$ / $\gamma$  interfaces for the two morphologies of  $\gamma'$  precipitates. The obtained results are discussed in the frame of possible solidification paths for this alloy.

## **Phase Characterization in Diffusion Soldered Ni/Al/Ni Interconnections**

G. Lopez<sup>1</sup>, P. Zieba<sup>2</sup>, S. Sommadossi<sup>1</sup>, W. Gust<sup>1</sup>, E.J. Mittemeijer<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Metals Research and Institute of Physical Metallurgy, University of Stuttgart, Seestr. 92, 70174, Stuttgart, Germany*

<sup>2</sup>*Institute of Metallurgy and Materials Science, Polish Academy of Sciences, Reymonta St. 25, 30-059 Cracow, Poland*

The formation and growth of intermetallic phases during a novel joining process based on diffusion soldering are presented. The Ni/Al/Ni bonds were accomplished due to isothermal solidification and subsequent interdiffusion of Ni and Al in the samples held at a temperature of 720 °C. Identification and characterization of the phases appearing at subsequent stages are widely discussed.

The application of optical and scanning electron microscopy, combined with the analytical capabilities of an electron probe microanalyser and X-ray diffraction technique allowed to characterize the microstructural changes as a function of reaction time.

The phases appeared in the following sequence: liquid Al → Al<sub>3</sub>Ni → Al<sub>3</sub>Ni<sub>2</sub> → AlNi (stoichiometric) → AlNi (Ni-rich) → AlNi<sub>3</sub>. At particular intermediate stages two or even four phases coexisted. The presence of two variants of the NiAl phase, namely a Ni-rich zone (60 at.% Ni) and stoichiometric AlNi is discussed in terms of the unusual interdiffusion processes of Ni and Al in the AlNi phase. The joining process was completed after 30 h of reaction with solely AlNi<sub>3</sub> compound to be present in the Ni/Al/Ni interconnection zone.

The quality of the resultant bond and the high melting point of the AlNi<sub>3</sub> phase (1360 °C) indicate a great potential of the diffusion soldering for the joining of heat dissipating elements used in electronics and electro techniques. On the other hand, no toxic materials are involved which makes the process environment friendly.

## **Study of Pyramidal Defects in Mg doped GaN and AlGa<sub>N</sub> Films**

R. Kröger, S. Frigge, T. Böttcher, and D. Hommel

*Institute for Solid State Physics, Bremen University,  
Kufsteiner Straße, 28359 Bremen, Germany*

GaN based films grown by metalorganic vapor phase epitaxy or molecular beam epitaxy for application in semiconductor optoelectronic and high power devices are meeting an increasing market. The combination of high hardness and heat resistivity with a direct band gap, needed for light emitters, makes it the material of choice for a large variety of applications. One threshold for success of GaN, the problem of p-type doping, seems to be overcome. Mg has been found to be a dopant with a ionization level of about 0.16 eV that can be introduced into the matrix material at levels of  $10^{19}$ - $10^{21}$  cm<sup>-3</sup>. It is found that p-type doping is facilitated by using AlGa<sub>N</sub> as semiconductor material. However, there are several problems to be solved: a sufficient activation of the Mg, which forms complexes with unavoidable process related hydrogen (usually by a post deposition anneal) and on the effect of Mg incorporation on the microstructure of the matrix material.

Recently<sup>1, 2, 3</sup>, it was reported that introduction of Mg leads to the formation of pyramidal shaped defects which are assumed to be non-radiative recombination centers. The nature of these defects has not yet been conclusively identified. This work gives a systematic study of properties like defect size and distribution using both Conventional and High Resolution Transmission Electron Microscopy (C/HRTEM) and investigates the correlation of the results with properties such as Mg diffusivity inside the matrix and possible reactions with the matrix material. These information are necessary to gain a deeper understanding of the nature of the defects and their dependency on deposition conditions. The investigation is performed for GaN and AlGa<sub>N</sub> at varying Mg concentration as well as for a variation of Al concentration at a fixed Mg level in AlGa<sub>N</sub>. First results show, that Al does not seem to have an effect on the defect formation. The pyramid basal plane coincides with the basal plane of the (0001) GaN and AlGa<sub>N</sub> and exhibits a hexagonal shape as found by plan-view TEM. The base diameter was between 5 and 15 nm and the density of the defects, as determined from cross section TEM, was around  $4.6 \cdot 10^{11}$  cm<sup>-2</sup>. This means that up to 20 % of the film area is covered by pyramidal defects.

Email: rkroeger@physik.uni-bremen.de

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## **Wheel-Rail Contact as a Source of Heat in Connection with Martensite Formation on the Railway Wheel Tread**

Vera Zahorova <sup>1)</sup>, Libor Benes <sup>2)</sup>

*University of Pardubice, The Jan Perner Transport Faculty*

*<sup>1)</sup> Department of Informatics in Transport, <sup>2)</sup> Department of Vehicles, Materials Section  
Studentska 95, 532 10 Pardubice, Czech Republic*

A railway wheel is the very important element of a railway vehicle. All normal and tangential forces having origin in weight of vehicle and freight, traction and braking affects are concentrated on the area just about 1 - 1,5 cm<sup>2</sup>. The phenomenon causes relatively fast degradation of the railway wheel tread. The materials changes, defects and even an accident of a vehicle can occur as a result.

Increasing of mass and running speed of railway vehicles is not possible without introducing any new technical solutions - replacement of block brakes by disc brakes is connected with this trend. But this change results in great number of damaged railway wheels.

Sliding of wheel along the rail is a quite common phenomenon, which has adverse consequences for the wheel and drastically increases the maintenance cost. The temperature rise caused by the skidding and the rapid cooling into the adjacent material when the wheel starts to roll again, may lead to formation of martensitic microstructure around the wheel flat. Martensite is a brittle phase and it has a crystal structure that leads to a volume expansion by approximately 0.5 percents as compared to the ambient pearlitic microstructure. This expansion results in very high compressive residual stresses in the martensitic structure and correspondingly high tensile residual stresses in the surrounding material. Presence of martensite often leads to cracking and spalling of the material.

Approximately 25 percent of all wheelsets that are taken out of service have spalls induced in consequence of presence of martensite. Therefore a better understanding of the mechanisms behind the formation of martensite around a wheel flat should be of great importance.

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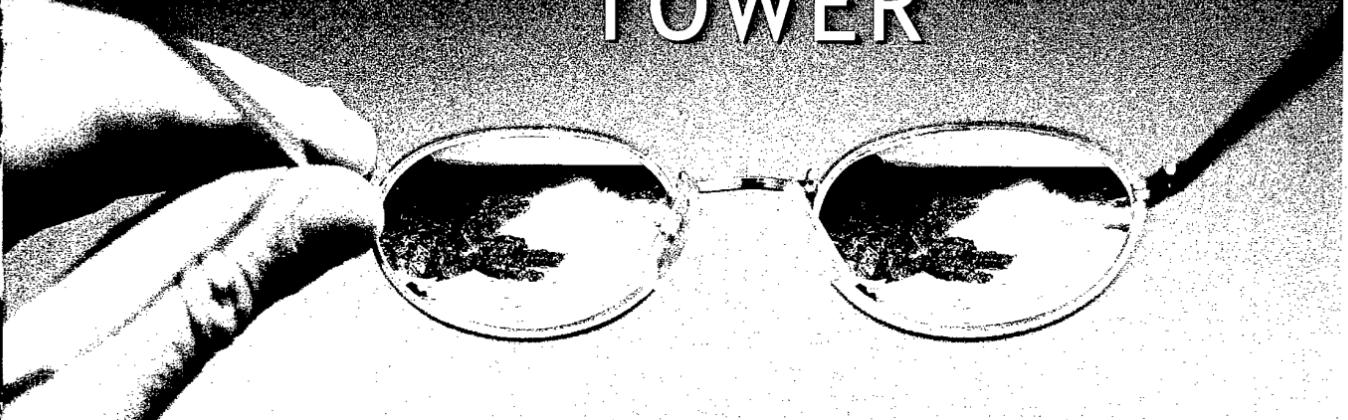
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